THE SUPERFICIAL OXIDES OF TITANIUM AT 950° AND 700°C.

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R. Kenneth Wolfe

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Approved:

Thesis Adviser

Date Approved by Chairman: June 30, 1956

PREFACE

Titanium, by virtue of its exceptional properties, is becoming increasingly important in our expanding technology. In view of this, the present investigation was designed as an examination of the superficial oxides which form at 950° and 700°C. in an atmosphere of oxygen at a pressure of one-tenth of an atmosphere. Emphasis was placed on the metallographic examination of the superficial oxides in situ and stripped.

The author is particularly indebted to Dr. R. J. Raudebaugh, who suggested the research, and to Dr. H. V. Grubb, whose advice and encouragement were indispensable to the direction of the research. In addition, the author wishes to express his gratitude to the School of Chemical Engineering of the Georgia Institute of Technology for the ready assistance in every phase of the present investigation, and to the Tennessee Eastman Corporation, which supplied two Fellowships.

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ABSTRACT

Titanium, popularly known as the dream metal, has become one of the most important and promising metals in metallurgical history. This fact has made the metal the object of highly concentrated research in the technological race that grips the United States. This research and interest is a natural result of titanium's properties: (1) Low density, (2) High corrosion resistance, (3) High temperature strength, (4) High yield, tensile, and ultimate strength and (5) Location and abundance of its ores, especially with respect to the United States.

To date, titanium's potential uses at high temperature have failed to develop because of its high reactivity with oxygen. Oxygen, in addition to ruining the metal's properties, depletes and eats up the metal by forming useless surface oxide scales at higher temperatures. This is ironical because it is this same reactivity between oxygen and titanium which gives to the metal its phenomenal corrosion resistance at room temperatures. At normal temperatures oxygen reacts with titanium to form an oxide barrier on the metal's surface which effectively prevents almost all corrosive media from reaching the highly reactive metal.

The superficial oxides of titanium have not been adequately studied or examined. Much work has been performed, however, on the titanium-oxygen system. Also, the kinetics of oxidation of high purity titanium has received considerable attention. Metallographically, the superficial oxides have been examined only once (Jenkins, A. E.) and this was a minor sideline to a kinetics study. The crystalline structure

of the high temperature superficial oxide has received minor consideration. None the less, the lack of knowledge about the superficial oxides leaves an information vacuum within which much can be contributed.

The present work, consequently, was an investigation of the superficial oxides formed at 950 and 700°C. in the presence of oxygen at a pressure of one-tenth of an atmosphere on commercially pure titanium and four commercially available alloys of titanium: MST111, RC130A, MST2Al-2Fe, MST2.5Fe-2.5V and MST3Al-5Cr. The present work was primarily concerned with a metallographic examination of the oxide films with X-ray diffraction playing a secondary role. This study was not another re-examination (repeat re-examination) of the rate of oxidation of titanium. More it was to be an examination of some of the physical properties of the oxide films to add new knowledge to the understanding of the superficial oxides and to elucidate and amplify the past kinetic studies.

In addition to stripping the thin oxide films of titanium for the first time, it is, ipso facto, the first extensive examination of these stripped films. While the present study is second chronologically to Jenkins in studying the thick oxide scales, it is the first extensive study and explanation of the various phenomena observed in the superficial oxides.

The objectives of the present study, in addition to finding a method of stripping the oxide, were to determine the physical characteristics of the oxides formed on titanium: (1) colors, (2) crystalline structure, (3) texture, (4) phases present, (5) variation of oxidation characteristics with alloy, (6) mechanism of oxidation, (7) uniformity of oxidation, (8) relations between metal structure and oxide structure, (9) presence of intercrystalline corrosion, etc.

To avoid the formation of spurious oxides, the titanium samples to be oxidized were heated in a high vacuum furnace prior to oxidation. The furnace was capable of maintaining the pressure below 0.02 microns during heating. The oxygen pressure during oxidation was maintained within plus or minus one mm Hg. and the temperature was maintained within plus or minus 22°C. of the desired temperature.

Metallographic examinations of the oxide and metal samples were performed on a Bausch and Lomb Research Metallograph. Both glancing angle and powder X-ray diffractions were performed with a North American Phillips Diffractometer type 12045B-1. Semi-quantitative analyses of selected oxides were performed on a 1½ meter grating spectrograph using arc excitation manufactured by Applied Research Laboratories.

The major conclusions of the study are outlined below:

1. Titanium dioxide (rutile) is the only superficial oxide detected on the titanium alloys studied by X-ray diffraction studies.

2. The superficial oxides of titanium undergo three distinct physical forms or stages of growth during the period when oxidation occurs: (1) Continuous tenacious film; (2) Small particles; and (3) Sintered particles.

3. The many colors exhibited by the superficial oxides of titanium, both when illuminated by fields of plane polarized and unpolarized light, were a function of the particles size of the oxides and, therefore, the degree of sintering and oxide strength.

4. The presence of blisters, strata, and loosely adherent scales in the oxides formed at 950°C. were the result of agglomerations of sintered particles breaking away from the core to relieve stresses which developed in the oxide.

5. The absence of blisters, strata, and loosely adherent scales in the oxides formed at 700°C. were due to a slow sintering rate, relative to the oxidation rate, which did not precipitate sufficient stresses to cause mechanical breakdown.

6. The visible structures present in the oxides were a reflection of vacuum etching of the titanium prior to oxidation.

7. The microstructure of the stripped oxides from alloys MST111 and RC130A which were formed during the early, and only the early, stages of oxidation at 950°C. were proven to be identical to the microstructure of the core.

8. Segments of the stripped and unstripped oxide films from alloys MST111 and RC130A at 950 and 700°C. formed during the early, and only the early, stages of oxidation gave a black and white reaction to polarized light; this reaction strongly indicates the presence of TiO at the metal-oxide interface.

9. The stripped oxide films possessed two types of overlapping layers that were discernable under a metallograph: (1) a thin transparent layer of nonporous and continuous crystals over a second layer of like structures and (2) a thin transparent layer of nonporous and continuous crystals over a second layer of small porous particles.

10. The oxide grows by the diffusion of oxygen through any nonporous superficial oxide that may be present and into the titanium core.

11. The oxidation laws and their irregularities reported by previous investigators are explained on the basis of the three physical forms of the oxide that are formed during oxidation.

12. The superficial oxides from all the alloys appeared similar in all major points; in the cases where dissimilarity ostensibly appeared - polarized light reaction in oxides from alloys MST 111 and RC130A at 950°C., overlapping crystals over similar crystals in the stripped oxides from alloy MST 111 at 950°C. and the reproduction of the core structure in the stripped oxides from alloys MST 111 and RC130A at 950°C. -- there is no evidence to indicate that these differences would not be erased (the oxides would appear similarly) by a more extensive study of the oxides formed during the initial oxidation periods.

CHAPTER I

INTRODUCTION

Titanium is popularly known as the "Dream Metal." No metal, in the history of metallurgy, has been the object of such great quantities of research as have been expended upon titanium. This fact would readily become evident to anyone upon examination of the metallurgical literature for the past seven years.

In terms of yield strength, tensile strength, and ultimate strength titanium is superior to most of the structural alloys in use. Because of its low density, titanium has the highest strength to weight ratio of all structural materials. By reason of its high melting point, titanium has promise of being used at unusually high temperatures. This promise has failed to develop to date because of its high reactivity -- especially with oxygen. Furthermore, this dream metal has phenomenal corrosion resistance at normal temperatures - in agitated sea water Rem-Cru's commercially pure alloy RC70 corrodes, without pitting, at a rate of only 0.001 inches in 1250 years (15).

Additional interest arises in the United States because of the abundance and location of the ores of titanium. This metal, which is the fourth most abundant of all the structural metals, would not have to be imported from across the seas to meet any demand created by a national crisis.

It seems not only suitable and timely, but essential to engage in basic research to further the knowledge about titanium. Accordingly, this

research initially was to be a study of the corrosion of titanium. Considerable information on the corrosion of titanium can be found in the literature and further extensive work in this area is being planned or performed. Furthermore, most of the corrosion investigators evinced a belief that the mode of protection was the formation and maintenance of an oxide film on the surface of the metal.

It seemed more apropos and opportune, then, to study the superficial oxide films of titanium. In addition, such an examination might elucidate the oxidation factors which limit the application of titanium at high temperatures.

A literature survey revealed that the oxides of titanium have been the subject of several investigations. The titanium-oxygen system has been studied by Ehrlich (6); Bumps, Kessler, and Hansen (4); and Rostoker (17). Ehrlich's analysis covered the system up to about 42 per cent oxygen by weight -- this corresponds to TiO_2. However, his titanium was not very pure, and he failed to discover the "delta" phase, later found by Bumps et al, which occurs below 925°C. at an oxygen composition of about 19 per cent by weight. Rostoker's work was performed to determine the effect of impurities on the titanium used by Ehrlich. He surmised that Ehrlich's work was essentially correct. The work of Bumps et al, was the most accurate since they used a higher purity titanium and they discovered a "delta" phase which was not discovered by Ehrlich. Their work was performed on the oxygen system up to about 33 per cent oxygen by weight which corresponds to a mixture of TiO and Ti_2O_3.

The rate of oxidation of titanium has been studied by several investigators. Davies and Birchenall (4) found the oxide film thickness

from 625° to 950°C. to be a linear function of time (linear rate law). Their rolled sheet titanium was oxidized in pure oxygen at one atmosphere pressure. They found Ti_2O_3 to represent the composition of the oxide despite the fact that X-ray studies indicated rutile to be the only oxide. Their work with chemically inert, radioactive tracers seemed to indicate that oxygen diffused in at least one phase (the outer layer) of the oxide scale by movement, probably, of oxygen anions through anodic vacancies. Hauffe and Pfeiffer's work (14) on the conductivity of TiO_2 containing some WO_3, MO_3 and LiO_2 also seems to indicate this mechanism. Jenkins (11) has studied the rate of oxidation on refined and commercially pure titanium in oxygen from 600° to 925°C. at a pressure of 700 mm mercury. He found the linear rate law to be applicable. Simmad, Spilners, and Katz (18) have studied the oxidation of oxygen saturated titanium and found the linear rate to be applicable after a nonlinear induction period. All of the above investigators manifestly neglected the initial periods of oxidation where the rate of oxidation was obviously nonlinear.

Gulbransen and Andrew (8) found that in the temperature range from 250° to 600°C. the oxide thickness was a "modified parabolic" function of the time of oxidation ("modified" parabolic rate law). Their high purity sheet titanium was oxidized in pure oxygen at one-tenth atmosphere pressure. Alexander and Pidgeon (1) found the film thickness to be a logarithmic function of time (Logarithmic rate law) in the range from 25°C. to 625°C. They used sintered and powdered titanium at pressures ranging from two to twenty centimeters of mercury. This is in disagreement with Gulbransen and Andrew; any differences being at least partially a function of the temperature ranges and the different physical forms of titanium employed

for the two studies. Waber (21) compounds the confusion by showing that Gulbransen and Andrew's data at 350°C. follows the cubic rate law (the film thickness is a cubic function of time).

Hickman and Gulbransen (8) made electron diffraction studies of oxides formed on the surface of titanium and its alloys of nickel, cobalt, and copper from 300°C. to 700°C. They found rutile (TiO_2) to be the only oxide present. Jenkins (12) and Davies and Birchenall (5) also have found rutile to be the only superficial oxide formed from 600 to 925°C. Richardsen and Grant (16) in the temperature range from 679° to 1012°C. by "Extensive X-ray studies of the surfaces of the specimens reacted with oxygen showed the presence of TiO_2 (rutile), TiO, and Ti."

Jenkins (12) has also reported some metallographic studies of the oxide cross sections formed from 600° to 925°C. on pure and commercially pure titanium. Morton (12), who examined the surface of titanium which had been oxidized in air, found NaCl type reflections. This may have been TiO but it could also have been TiN.

Based on the literature survey, the decision was made to make thorough investigations of the superficial oxides formed on titanium at 700° and 950°C. The temperatures were chosen to be above and below the allotropic transformation which occurs at 882°C. Oxidation was to be in pure oxygen at a pressure of one-tenth atmosphere. Commercially pure titanium and four of its commercially available alloys were employed.

As an objective, the studies were an attempt to determine and explain some of the physical characteristics of the surface oxides such as color, crystalline structure, variation of oxidation characteristics with alloy, phases present, texture, etc. Since all previous studies of

oxidation have been almost exclusively kinetic and diffraction studies with one minor exception (Jenkins), it was decided that this study was not to be just another oxidation rate diffraction study. Rather, this study was to be a fundamental examination of the superficial oxides to obtain new information and, possibly, to obtain information that would elucidate and clarify the previous oxide studies.

The examinations were made using principally a research metallograph. Visual examination, X-ray diffraction and spectrographic studies were employed in a supporting role.

The technique for stripping thin films developed by Nurse and Wormwell (13) was used, for the first time, to strip the thin oxides from titanium.

CHAPTER II

EXPERIMENTAL METHODS

The information necessary to understand and to repeat the present studies is explained in the ensuing chapter.

Equipment

The major pieces of equipment - vacuum furnace, X-ray equipment, electropolisher, metallograph, and spectrograph - are described below.

Vacuum furnace--A high-vacuum furnace, schematized in Figure 1, was used to prevent the formation of spurious oxides during the process of heating titanium samples to the oxidizing temperatures. The "Two-Inch Ceramic Tube Vacuum Furnace Assembly for High Vacuum Metallurgy" was obtained from Consolidated Vacuum Corporation, formerly known as Distillation Products, Incorporated, of Rochester, New York.

This vacuum furnace proved to be totally inadequate and was modified to improve the ultimate vacuum obtainable. To do this, the DPi type VMF 20 diffusion pump was replaced with a National Research Corporation H-2-P type 113 diffusion pump. The roughing fore pump was a Welch mechanical pump type 1403. Also, a vycor tube was substituted for the ceramic tube and was utilized as an oxidation and heating chamber. The vycor tube was connected to the pumping system by a three-quarter inch copper tube. This junction between the vycor tube and the copper tube, as well as other joints in the vacuum system, was made vacuum tight with Apiezon Wax. The oxidation chamber was isolated from the pumping system to protect the pumping fluids during oxidation by a Hills McCanna type 500A diaphragm

valve located in the copper tube. The pumping system evacuated a total volume of about 150 cubic inches.

A 20 liter carboy, connected to the vacuum furnace through a stopcock, was employed as a reservoir to store oxygen prior to and during oxidation. That is, the volume of oxygen was so large that depletion by oxidation was negligible and the pressure did not vary more than plus or minus one millimeter.

The temperature fluctuation in the section of the furnace used for heating and oxidizing was plus or minus 22°C. at 950°C. and plus or minus 11° at 700°C. Temperature control was maintained by Wheelco's Model 224 pyrometer which was an "On" and "Off" controller.

The low pressures in the vacuum furnace were measured by a DPi type PHG-1 Phillips Ionization gauge. The gauge was factory calibrated to read dry air pressures from 2.5 hundredths to 25 microns of mercury.

The pressure maintained in the vacuum furnace at 950° and 700°C. was below 2.5 hundredths of a micron of mercury -- the lowest pressure indicated by the pressure gauge. Titanium samples heated to 950°C., removed and quenched to room temperature in an atmosphere of argon appeared very bright with no oxide films that could be observed visually or under the metallograph. This was sufficient evidence that negligible oxidation took place. In fact, the surface after such treatment was vacuum etched. Vacuum etching, which will be discussed later, occurs by preferential evaporation from the metal grains according to their orientation.

X-ray equipment--X-ray diffraction studies were performed with a North American Phillips Diffractometer type 12045B-1. Both a geiger counter with automatic recording and a Debye Scherrer camera were employed.

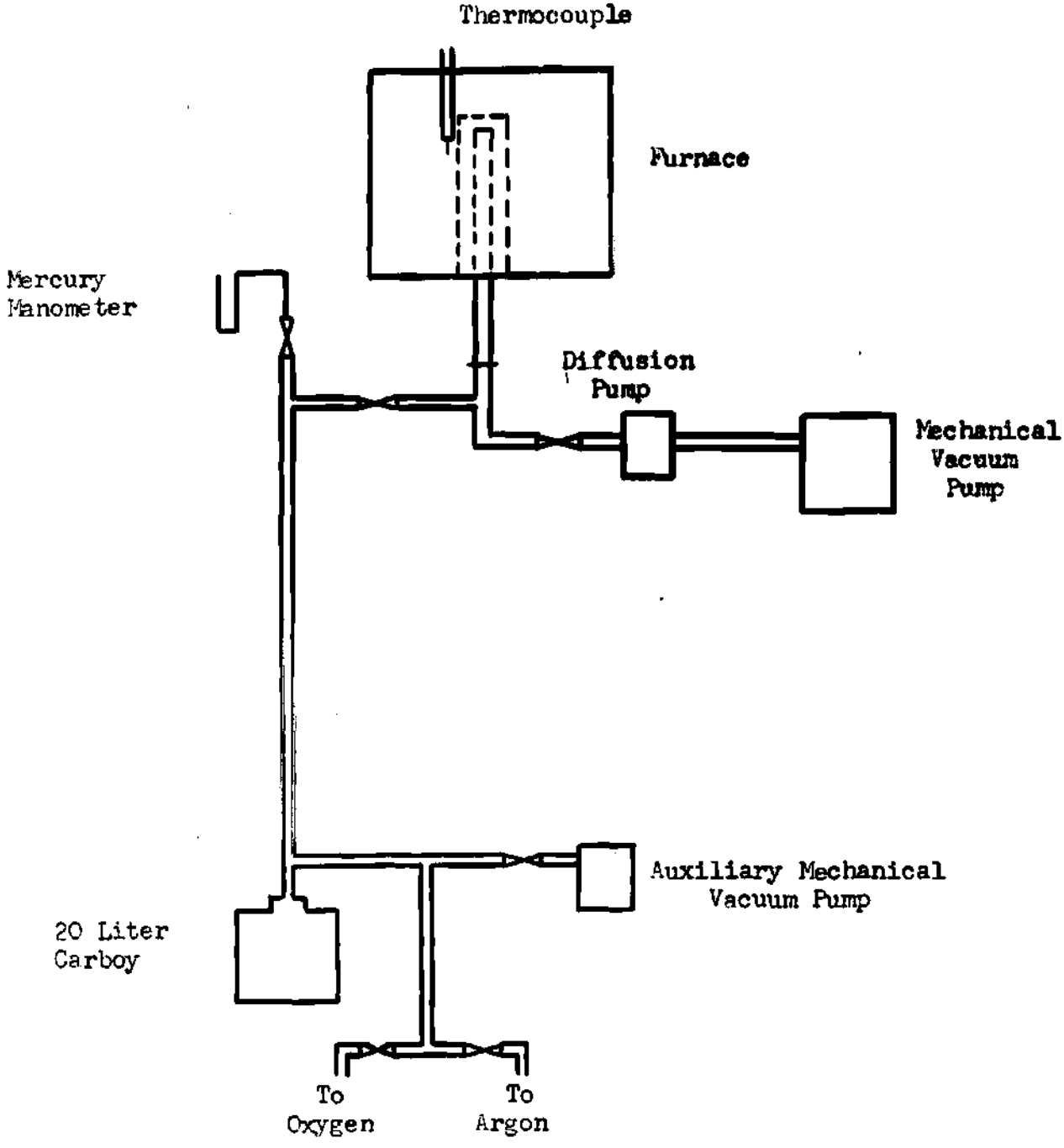


Figure 1. Schematic Representation of the High Vacuum Furnace

Electropolisher--An excellent Disa Electropolisher, manufactured by H. Struers Chemiske Laboratorium of Copenhagen, Denmark, was employed for electrochemical polishing.

Metallograph--A Bausch & Lomb Research Metallograph was employed for optical observations at high and low magnifications. This instrument combined in one assembly facilities for optical observations and photomichrography with bright field, dark field, and polarized field illumination at magnifications up to 2100 power. A lens-free Leica 35 mm camera was attached to a monocular eyepiece of the metallograph for making Kodachrome micrographs. A tungsten arc was used as the light source.

Spectrograph--Semi-quantitative analysis of the films was made on a 1½ meter grating spectrograph using arc excitation. This spectrograph was manufactured by Applied Research Laboratories, Glendale, California.

Alloys and Oxides

Experimental alloys--Unalloyed titanium and four alloys of titanium were utilized in this study: (1) MST 2Al-2Fe, (2) MST 2.5Fe-2.5V, (3) MST 3Al-5Cr and (4) MST Grade 111 (Commercially pure), manufactured by Mallory-Sharon Titanium Corporation, Niles, Ohio; and (5) alloy RC-130A, manufactured by Rem-Cru Titanium, Inc., Midland, Pennsylvania. These alloys were hotrolled and annealed by the manufacturers. Photomicrographs of these alloys are given in Figures 2, 3, 4, 5 and 6.

Some physical properties of the known titanium oxides--A brief summary of physical properties of the known oxides are presented in Table 1. Presented are the melting points, molecular volume, reaction to polarized light, partial free energies of decomposition at 1000°C. and the ratio of the oxide molecular volume to that of titanium.

TABLE 1

SOME PHYSICAL PROPERTIES OF TITANIUM AND ITS KNOWN OXIDES

Compound	Stability (9) °C.	Structure (9)	Melting Point (9) °C.	Partial Free Energy per Mole O_2 (10)* kcal.	Atomic Volume (9)** cms.	Volume Ratio (9)***	Reaction to Polarized Light
Ti alpha	Below 883	Close packed hexagonal			10.8		Reddish brown to slate-blue
Ti beta	Above 883	Body centered cubic	1730		11.1		
TiO alpha	Below 990	Cubic, NaCl			11.0/13.0	1.20	Black to white (4)
TiO beta	Above 990		2020	-176			
Ti_2O_3 alpha	Below 200	Cr_2O_3			30.5/32.0	1.48	
Ti_2O_3 beta	Above 200		2130	-174/-126			
Ti_3O_5 alpha	Below 177	Orthorhombic			52.1/53.4	1.64	
Ti_3O_5 beta	Above 177			-126/-87			
TiO_2 rutile	Above 915	Tetragonal, SnO_2	1860	-50	18.8	1.73	
TiO_2 anatase	Below 915	Tetragonal			19.3	1.78	
TiO_2 brookite	Unstable	Orthorhombic	1900 (4)		19.8/20.5	1.89	

*Where discontinuities in the partial free energies occur, the values just below and just after the discontinuity are given; the value for the lower oxygen content is given first.

**Since some of the oxides of titanium form structures with vacant lattice sites, the densities determined from X-ray data are higher than those determined by direct measurements; both values are given above with the X-ray value given first.

***The ratio given is the measured volume of the oxide divided by the volume of alpha titanium for an equal amount of titanium.

Chemical analysis and physical tests performed by the manufacturers on these alloys are given in Table 2.

Experimental Procedure

The more important experimental procedures are described in this section.

Sample preparation--Titanium samples, one-half inch square, were prepared for oxidation by chemically cleaning the surface to avoid any extraneous factors which might influence the oxide products. Cleaning by electrochemical polishing and chemical methods were compared in preliminary studies and were found to be equivalent. Because of the greater ease of application, the chemical cleaning was used. This cleaning consisted of dipping the samples for a few seconds into a solution of 8% nitric acid (AR), 2% hydrofluoric acid (AR), and 90% water by volume at a temperature of 140°F. After cleaning, the samples were rinsed in absolute ethyl alcohol and dried in a stream of warm air from a "hand" hair dryer. The resulting surface was found to be clean and fairly smooth when viewed optically on the metallograph at 250 power.

Oxidation--The samples were oxidized in the high vacuum furnace after being heated to the desired temperature, either 950°C. or 700°C. The auxiliary storage carboy contained enough oxygen to give one-tenth atmosphere pressure during oxidation; for long oxidation periods the oxygen was occasionally augmented to maintain the pressure within plus or minus one millimeter of the desired pressure. During oxidation the pumping system was isolated from the oxidation chamber by closing the diaphragm valve located between the two sections. Oxidation commenced when oxygen from the storage carboy was injected into the oxidation

TABLE 2

THE COMPOSITION AND PHYSICAL PROPERTIES OF THE EXPERIMENTAL ALLOYS

	MST 2Al-2Fe		2.5Fe-2.5V		3Al-5Cr	MST111		RC130A
Heat No.	26L65A4		31H37A3		29F19A2	20237		A5231
Carbon	.78		.74		.52	.04		.15
Nitrogen	.030		.038		.086	.043		.02
Iron	3.45		2.28			.37		
Aluminum	2.19				1.93			
Chromium	.05				5.38			
Vanadium			2.55					
Nickel								
Mn								10.9
	Long.	Trans.	Long.	Trans.		Long.	Trans.	
Hardness								
Rockwell						A 60		
Brinell	RA 69.5	70	64.0	64.5	BRITTLE			
Olsen								
Bend						2T	2T	2.9T
Yield Lbs. Per Sq. In.	133,700	133,800	111,100	122,300		75,800	78,100	145,300
Ultimate Lbs. Per Sq. In.	151,700	139,100	145,500	146,300		94,200	90,000	158,000
% Elongation	1.6	3.1	5.5	4.7		23.4	23.0	8.5

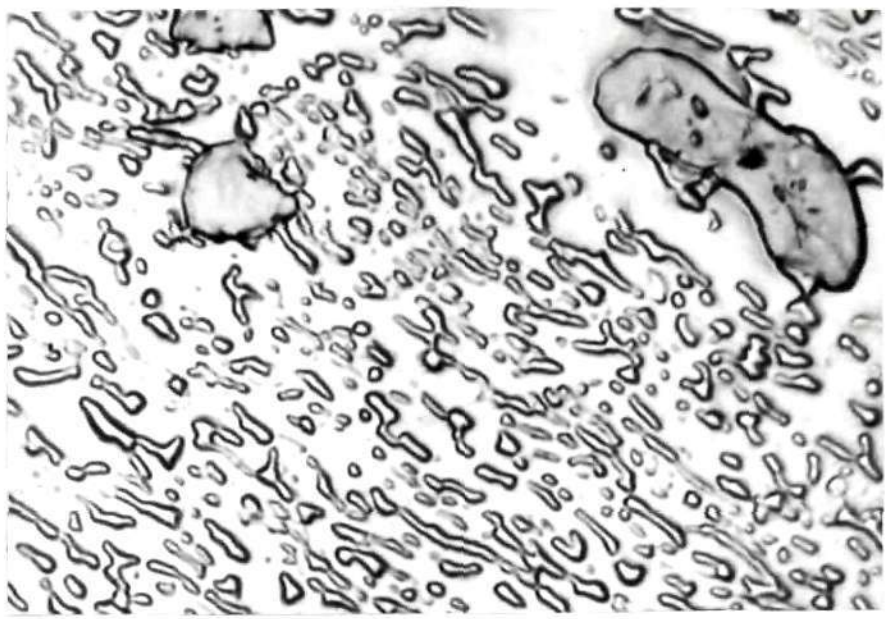


Figure 2. The Structure of Hot Rolled and Annealed MST 2Al-2Fe. The structure shows small beta grains and a few titanium carbide particles in a matrix of alpha. X1000 and enlarged twice, electrochemically etched.

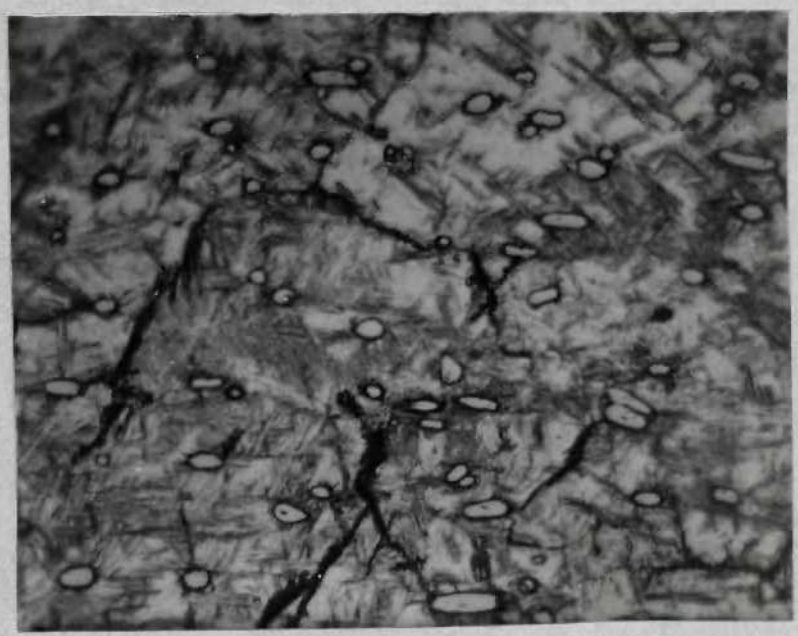


Figure 3. The Structure of Hot Rolled and Annealed MST 2.5Fe-2.5V. The structure shows titanium carbide particles evenly dispersed in an ascicular alpha transformation product. The prior beta grains are outlined. X500, electrochemically etched.

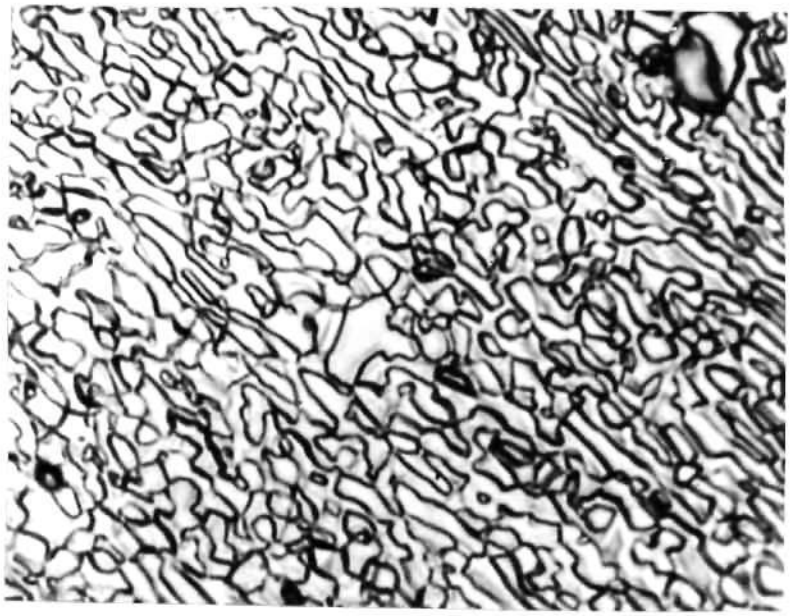


Figure 4. The Structure of Hot Rolled and Annealed MST 3Al-5Cr. Alpha grains and titanium carbide particles are evenly dispersed in a beta matrix. This alloy, as shown by macro etching, possessed a highly inhomogeneous structure. The influence of rolling was clearly evident in the hetergeneous structure - See Figure 18. X1000 and enlarged twice, electrochemically etched.

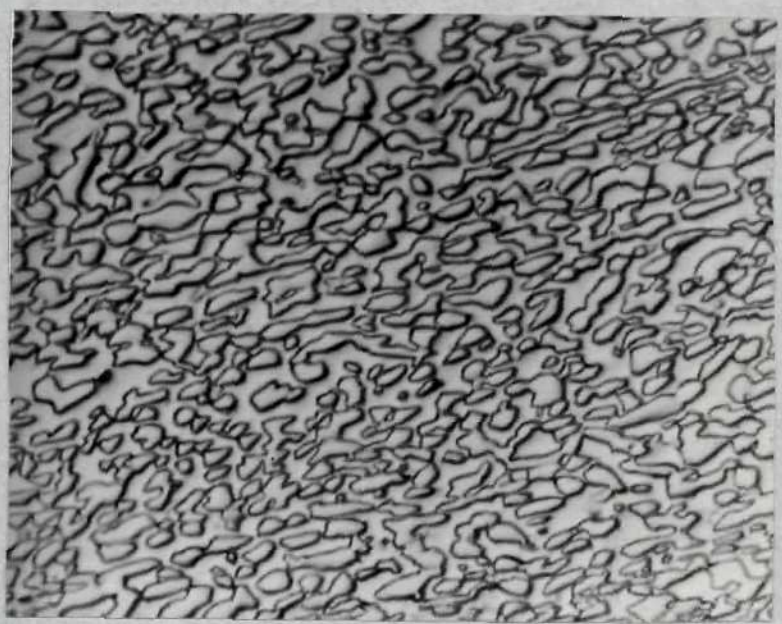


Figure 5. The Structure of Hot Rolled and Annealed RC130A. The micrograph shows alpha grains in a beta matrix. Macroetching showed this alloy to be highly inhomogeneous. The macro structure clearly indicated the influence of rolling - See Figure 18. X750 and enlarged four times, electrochemically etched.

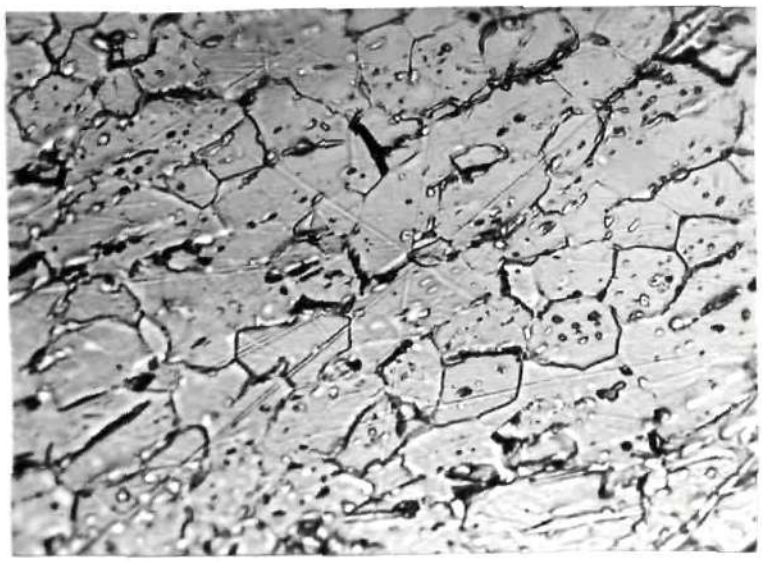


Figure 6. The Structure of Hot Rolled and Annealed MST 111. The micrograph shows small beta particles dispersed throughout a matrix of equiaxed alpha. X1000, electrochemically etched.

chamber. Oxidation was terminated by evacuating the oxidation chamber with an auxiliary mechanical pump. Immediately after stopping oxidation the chamber containing the samples was removed from the furnace and air cooled (cooling required about 15 minutes) to room temperature while a stream of argon was fed into the chamber. The oxidation time was measured from the moment of initial contact with oxygen until the chamber was evacuated.

Metallographic preparation--The oxide and metal cross sections were mounted together for metallographic preparation in a polyester resin. The resin hardened at room temperature upon the addition of an "accelerator" and a "hardener". Mounting in this manner avoided the high temperatures and high pressures normally encountered. High temperatures and pressures have been known to precipitate misleading structural changes in titanium.

By reason of titanium's tendency to smear and drag, mechanically polished titanium samples possessed a thin surface layer of cold worked material. It was expedient to remove this spurious structure by augmenting the "fine" stages of mechanical polishing with electrochemical polishing. The following solution was used for electrochemical polishing with the Disa-Electropolisher: 590 cc methyl alcohol, 350 cc butylcellosolve, 60 cc perchloric acid (density 1.60) and 2 cc of "Solvent X" (obtained from Uddeholm Company of America). The applied potential was 30 to 50 volts and the polishing time was dependent upon the extent of the prior mechanical polishing.

The time of the electrochemical polish had to be short; otherwise, the edges of the resulting sample were rounded. This made photomicrography and micrography of the edge impossible. However, the "fine"

mechanical polishing promoted some rounding of the edges and, as a result, had to be short. The mechanical polishing time, therefore, from No 400 carborundum through No 600 carborundum and levigated alumina was shortened to a total of ten seconds or less. The subsequent electrochemical polish took from 1 to 3 seconds. The ensuing edge was found to be excellent for observation.

The oxide cross sections were prepared metallographically by rough grinding on No. 180 emery paper and then polishing for a few seconds on a felt cloth which contained levigated alumina suspended in water for an abrasive. This short polishing procedure rendered the oxide detail better than that obtained when using the extended polishing normally employed. Normal polishing left the soft oxides highly undulated since they were softer than the surrounding mounting material and the titanium metal.

Film stripping--Stripping of the thin tenacious surface film was implemented by dissolving away the metal in a bromine-methanol solution. The bromine-methanol solution contained ten cubic centimeters of chemically pure bromine and 90 cubic centimeters of chemically pure methanol. The methanol was distilled over magnesium to keep the water content to a minimum. The film was preserved by adhering the oxide to a glass slide prior to stripping. The titanium sample, freed when necessary of any loose oxide scale, was cemented to a glass slide with pliolite dissolved in kerosene, after which the kerosene was slowly evaporated in an oven at 60°C. The metal was exposed for subsequent chemical attack by grinding away the impervious thin film on the surface opposite, not adjacent, to the glass slide. The slide and sample was then placed in the bromine solution. Stripping was accomplished in

about three to four hours. The freed film was washed in methanol prior to examination on the metallograph.

Many of the films were lost during stripping due to poor adherence to the glass slide. This accounts for variations in the number of stripped oxides reported in the Tables for each alloy.

In preliminary studies the effect of water and oxygen on the oxide film during stripping was unknown. Rigorous steps were taken to eliminate these factors. During stripping argon was bubbled through the bromine solution to keep the solution free of oxygen. However, films stripped in untreated solutions appeared equivalent to films stripped in treated solutions. As a result, the technique employing an atmosphere of argon was abandoned.

Photographic techniques--Kodak Metallographic plates -- orthochromatic, antihalation of high green sensitivity -- were used to produce black and white negatives. The emulsion on this plate was capable of high resolving power and very high contrast.

Kodachrome transparencies and positives were processed by Eastman Kodak Company.

X-ray and spectrographic studies--Mr. William E. Woolf, Research Physicist at the Engineering Experiment Station, Georgia Institute of Technology and Dr. William M. Spicer, Director, School of Chemistry, Georgia Institute of Technology, performed and interpreted X-ray and spectrographic studies respectively. Both powder and glancing angle techniques were used in the X-ray studies.

Metallography

Figure 7 presents a basic diagram (3), useful for discussing the metallography of titanium, and a portion of the titanium-oxygen system (4).

The alpha phase is close-packed hexagonal and the beta phase is body-centered cubic.

Alloying additions are classified according to their effect upon this basic diagram. Alloying additions affect the phase diagram by stabilizing either the alpha or the beta phase. Stabilization occurs when the temperature range and the composition range, over which the phase is stable, is increased. Some alpha phase stabilizers are carbon, oxygen, nitrogen and aluminum. Typical beta phase stabilizers are hydrogen, manganese, chromium, molybdenum, iron, vanadium and cobalt.

At 950°C. the beta phase is stable up to an oxygen content of about 0.35 per cent. Alpha and beta phases co-exist from 0.35 per cent to 1.6 per cent oxygen. The maximum oxygen concentration in the alpha phase is about 14.5 per cent.

The allotropic transformation which occurs in titanium provides a number of microconstituents whose appearance depends upon the heat treatment and composition. The structure can consist of any combination of alpha, beta, and the many transformation products (mixtures of alpha and beta). Of course, interstitial and intermetallic compounds, such as titanium carbide, are present in titanium alloys.

Metallographic interpretation of the phases of titanium was aided by the optical anisotropic property of the alpha phase. This property is typical of metals which possess unsymmetrical crystalline structures. Accordingly, the alpha phase, when illuminated by plane-polarized light, exhibited four changes in color upon being rotated through 360°. When using the Bausch & Lomb Research Metallograph, there were two color transformations from brownish-red to slate-blue at azimuths of 0° and

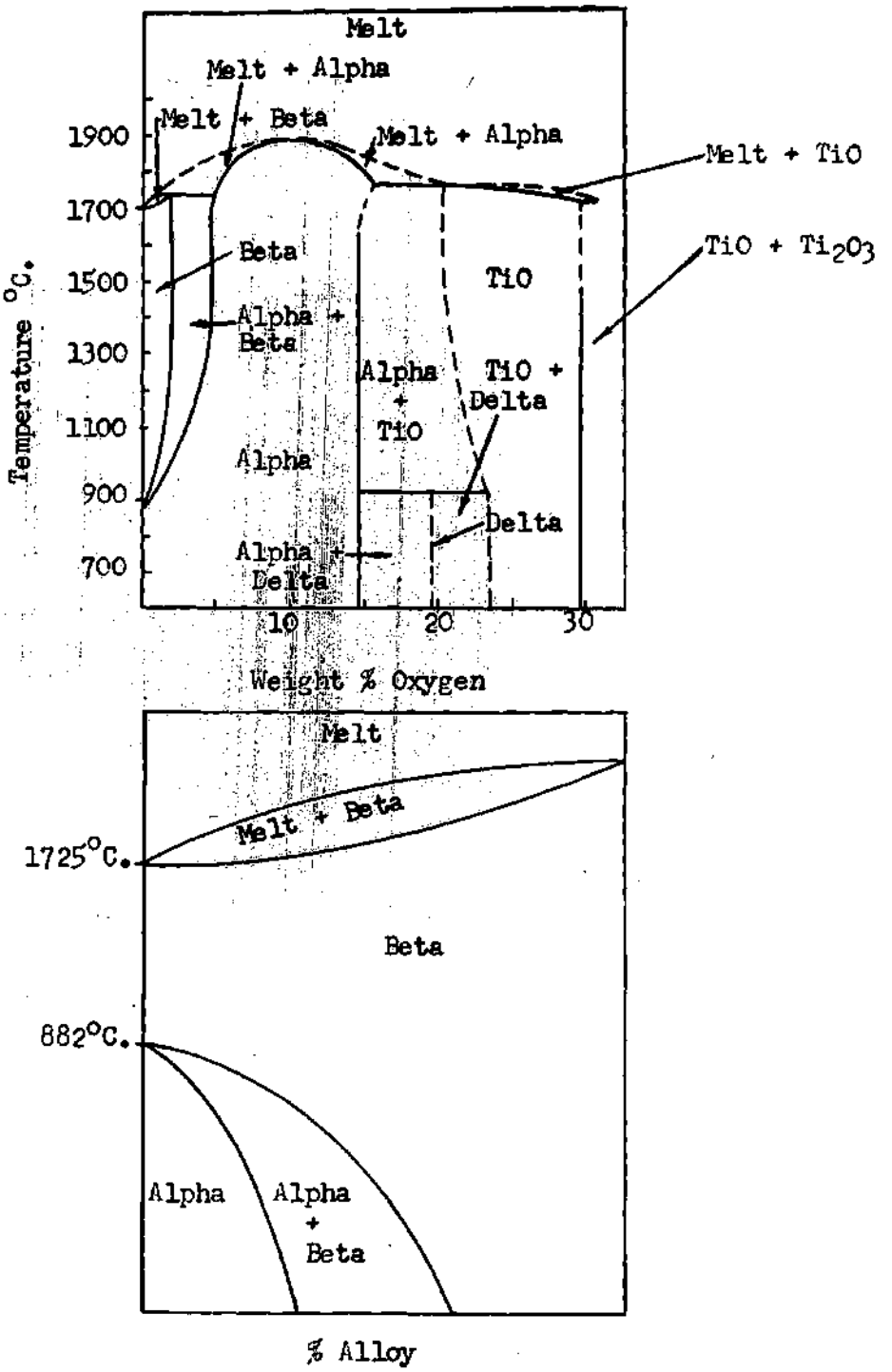


Figure 7. Partial Phase Diagram for Titanium-Oxygen System and A Basic Phase Diagram for Titanium

180° and two transformations from slate-blue to brownish-red at azimuths of 90° and 270°.

These polarization colors could be somewhat different with other metallographs since the color is dependent upon the quality of the lens system. The objective lenses used in the Bausch & Lomb Research Metallograph were achromats. As such, they were corrected spherically and chromatically for only the green-yellow region of the spectrum and were incapable of true color rendition.

The beta phase, which was body-centered cubic, characteristically was optically isotropic and remains dark when rotated in a plane-polarized field.

Titanium oxides appeared as brilliant mono-colored or multi-colored layers when illuminated by polarized light. Metallographic examinations and comparisons were made immeasurably easier by this fact. When viewed under ordinary bright light, the oxides appeared as narrow dark bands because they reflected little light. Metallographic examination of structural detail was impossible. However, under polarized light the glare of the titanium sample was removed and the oxide detail was revealed.

CHAPTER III

RESULTS

The data obtained from examinations made with the research metallograph, X-ray diffractometer and spectrograph are recorded in the tables which appear in the Appendix. These tables are described in this chapter.

Superficial Oxides and Core

The data obtained from observations of the titanium superficial oxides and the titanium core are presented in Tables 4 - 21 which are placed in the Appendix. The following information, which was obtained from optical and visual observations is presented: (1) time of oxidation, (2) polarization colors, (3) film thickness, (4) film characteristics, and (5) metallographic description of the titanium core.

Polarization colors--The various colors exhibited by the oxide cross sections when illuminated by plane polarized light are recorded. The colors are tabulated in the same sequence as they occur in the film beginning with the oxide surface and proceeding to the oxide-metal interface.

Film thickness--Film thicknesses are recorded to the nearest thousandth of an inch. The thickness was not recorded unless it was substantially one-thousandth of an inch or more.

Film characteristics--Recorded for characterization of the oxides are several interesting features: (1) visual color or colors, (2) adherence, (3) texture -- presence of sintered particles, voids, fissures, strata, blisters, etc., (4) visual grains, (5) inhomogenities, and (6) number of layers.

The column headed Film Characteristics is subdivided into two sections. In some instances, oxide scales formed on titanium were completely nonadherent to the core (these films were held in place since they formed a shell around the core) or were so loosely adherent that they could be removed easily by mechanical means (scraping, shearing with a razor blade, etc.). Under these loose outer layers, tenaciously adherent to the titanium core, was a core oxide or core layer. For this reason, the column headed Film Characteristics was subdivided into two sections when appropriate: the outer layer and the core layer.

Metallographic description of sample--A metallographic description of the cross section of the titanium core is given. Observations showed that two metallographically different areas were present in the sample. As a result, the description was subdivided into two sections: the edge and the center. The thickness of the edge layer is reported to the nearest thousandth of an inch.

Stripped Films

Data obtained from optical examinations of the stripped oxide films are presented in Tables 5-21. Information on the (1) grain size, (2) grain shape, (3) uniformity, and (4) type of film are presented. The column headed "Comments" gives additional self-explanatory information.

The numbers given in the column headed "Grain Size" represent the number of grains present in one square inch at the given magnification. For instance, six grains per square inch at a magnification of 1,047 diameters would be represented as 6/1,047.

The type of micrograph refers to two features of interest: the sharpness of the grain boundaries and the presence of overlapping grains.

X-ray Diffraction

The results of X-ray diffraction studies presented in Table 22 show that TiO_2 was the only superficial oxide that was detected. To assure that no other oxide was present, the film from alloy MST 111 which was oxidized for nine hours was given several successive polishing treatments to remove small quantities of the film. This treatment was continued until the core metal was reached. After each polishing treatment an X-ray diffraction was taken. No difference in the diffraction patterns could be detected. The oxide from MST 111 which was grown for 45 seconds was subjected to X-ray diffraction and only TiO_2 was found.

Spectrograph

Data from spectrographic studies are presented in Tables 23 and 24. The results show the semi-quantitative analysis of various oxides.

CHAPTER IV

DISCUSSION

The experimental results are discussed, examined and organized in the ensuing chapter.

Oxide Forms

The superficial oxides of titanium undergo, as indicated by the experiments, three distinct physical forms or stages of growth during the period when oxidation occurs. These forms are: (1) Continuous film; (2) Small particles; and (3) Sintered or fused particles. These forms are shown in Figure 8. While Jenkins (12) understood the film from density studies to be porous, he failed completely to understand the nature of this porousity. Furthermore, he failed to observe the small particles and the three stages of oxide growth. He mentions only "natural rock strata".

Continuous film--In the initial stage of oxidation, a thin film formed on the surface. This film, which grew by diffusion of oxygen into the metal, was thin, continuous, nonporous and always exhibited Newton's interference colors. Moreover, the film in this stage was always very tenacious. The film structure during this initial stage is depicted in Figure 9.

Small particles--As the oxidation process was continued, loose powdery particles appeared on the surface of the film as shown in Figures 10 and 11. These particles were extremely small in size. Their appearance

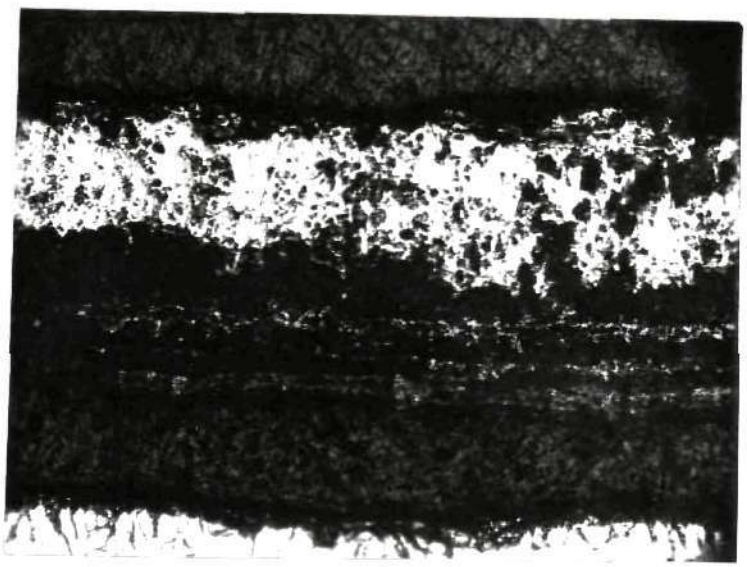


Figure 8. The Three Superficial Oxide Forms. The photomicrograph presents a typical oxide cross section which, in this case, was grown for 18 hours at 950°C. on alloy MST 2Al-2Fe. X100

Figure 9. Typical Thin Continuous Film. The picture depicts a typical thin film from alloy MST 111 grown for three minutes at 950°C. (the film is shown on the surface). The film, which displays the grain luster phenomena, is identical to the structure of the metal core. Higher magnifications reveal that the grains are composed of smaller grains in many cases. X100.

Figure 10. Incipient Particle Formation. Shown here is a typical surface of an oxide film grown for three minutes at 950°C. on alloy RC130A. The structure, which possesses the well-known grain luster phenomena and is a reproduction of the metal core structure, shows the initial formation of small isolated segments of small particles. X100.

Figure 11. Small Particles. Pictured in the micrograph is a typical oxide composed of small particles. This particular oxide, which displayed a bright yellow color, appeared on alloy MST 2Al-2Fe after oxidation for three minutes at 950oC. X100.

on the film marked the onset of the second stage in the oxidation process, which may be characterized appropriately as the small particle stage. During this stage the oxides appeared charcoal, gray, white and bright yellow.

Continuous film growth, by reason of the differences in the density of the oxide and of the metal core, caused stresses in the oxide. In accordance with Le Chateller's Principle, the film reacted in such a way as to undo the effect of the stresses. In the reaction of the film, completely new grains which were smaller and strain free were formed. The recrystallization of the grains in order to relieve stresses was similar to annealing.

For each increment in film thickness there was a simultaneous increase in the film stresses. The continuous undoing of the stresses, therefore, resulted in continued recrystallization and consequent subdivision of the grains. The process continued until the film became a porous mass of small particles which were essentially strain free.

Sintered or fused particles--The small particle structure formed in the preceding stage ultimately was sintered into still larger particles. Some grains formed by sintering are shown in Figure 12. The visual colors shown by the oxides during this stage of growth are yellow, brown and slate gray.

The sintering mechanism, which also strengthened the oxide, was confirmed experimentally. Several titanium samples, placed side by side so that they touched, were subjected to oxidation for 18 hours at 950°C. The resulting oxide products were sintered together and the fact that their origin was from two different samples proved the sintering hypothesis.

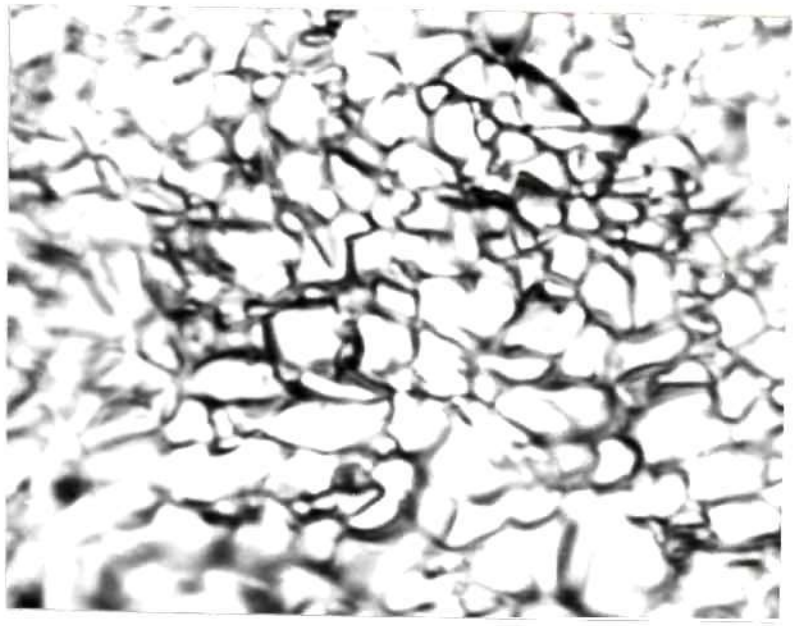


Figure 12. Sintered Particles. The structure shows sintered particles which appeared on the surface of an oxide formed on alloy MST 2.5Fe-2.5V for five hours at 950°C. X500 and enlarged four times.

Visual and Polarization Colors

Many colors were displayed by the oxides. Some of these colors, which were observed under polarized light, are reproduced in Kodachrome micrographs in Figures 13, 14 and 15. These micrographs are of oxide cross sections from all five alloys grown for 20 hours and from alloy MST 3Al-5Cr grown for 15 hours at 950°C. and are shown for comparison. These reproductions represent fairly but not perfectly the various oxide colors.

The oxide colors, seen using both bright-field and polarized illumination, are related to the oxide particle sizes. This hypothesis was confirmed experimentally. Some slate-gray oxide scales, which are composed of large fused particles, were pulverized with a mortar and pestle. A change in visual color from slate-gray to brown accompanied the resulting particle size reduction. Continued pulverization brought about a yellow color in the ground oxide. Further color changes were not achieved by this technique, but the color changes that were obtained by mechanical particle size reduction were sufficient to confirm the hypothesis. These colors are a manifestation of the more widely known "Tyndal Effect." Furthermore, since the degree of sintering and, therefore, the particle size are a measure of the oxide strength, the color of the oxide is also a measure of the oxide strength.

Davies and Birchenall (5) explained the various colors on the basis of varying oxygen content in the TiO_2 lattice.

The particle size increased with the following sequence of polarization colors: (1) Gray, (2) Blue-white, (3) White, (4) Light-yellow, (5) Orange, (6) Red, and (7) Blue to dark blue. Likewise, the particle size for visual colors increased with the following sequence: (1) Charcoal, (2) Gray, (3) White, (4) Bright-yellow, (5) Yellow, (6) Brown, and (7)

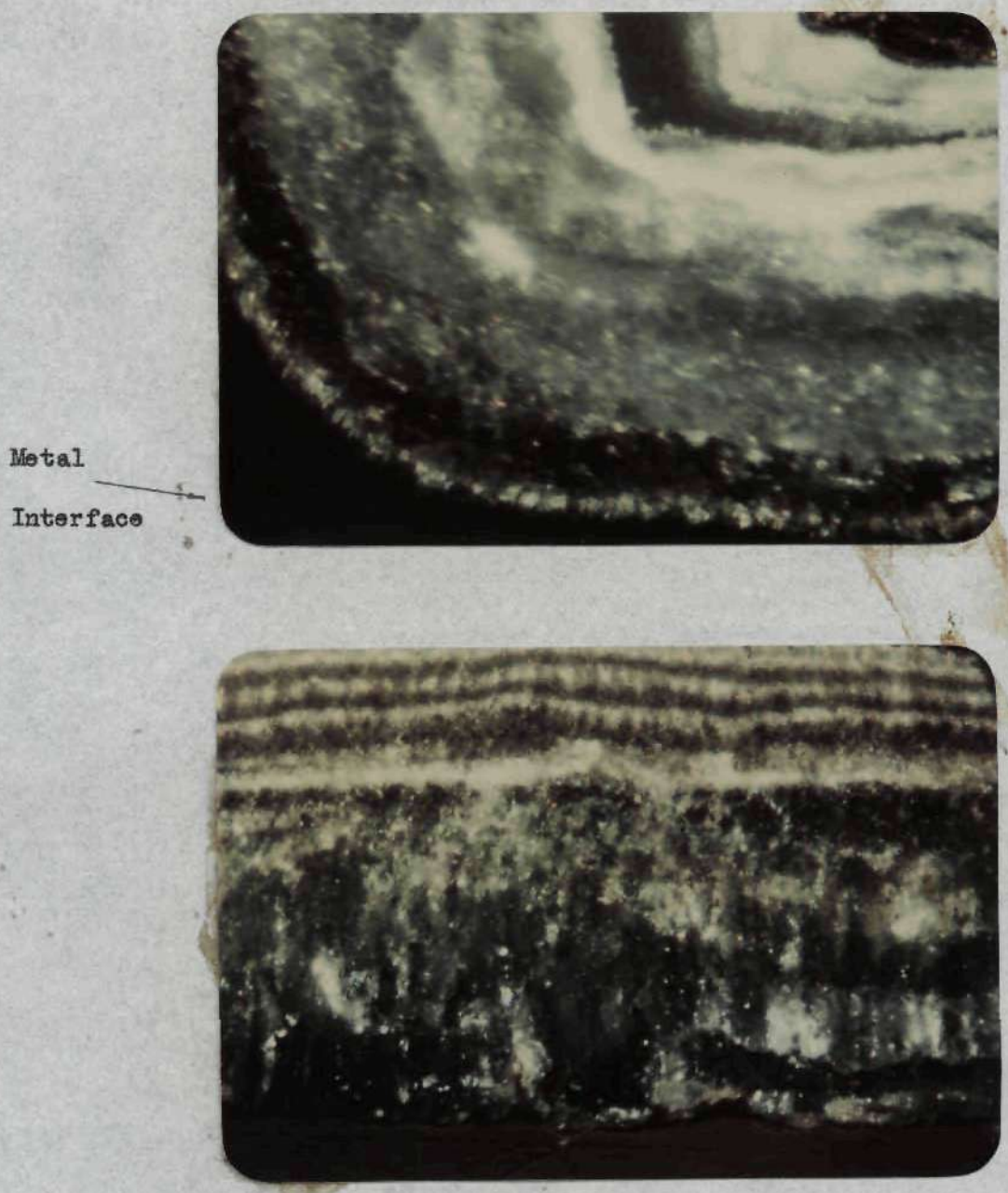


Figure 13. Kodachrome Micrographs. These pictures, which have too much green in them, show the oxides from (a) MST 111 and (b) RC130A which were grown for 20 hours at 950°C. The lower sections represent the oxide that was adjacent to the metal core. (a) X86 and enlarged three times; (b) X49 and enlarged three times.

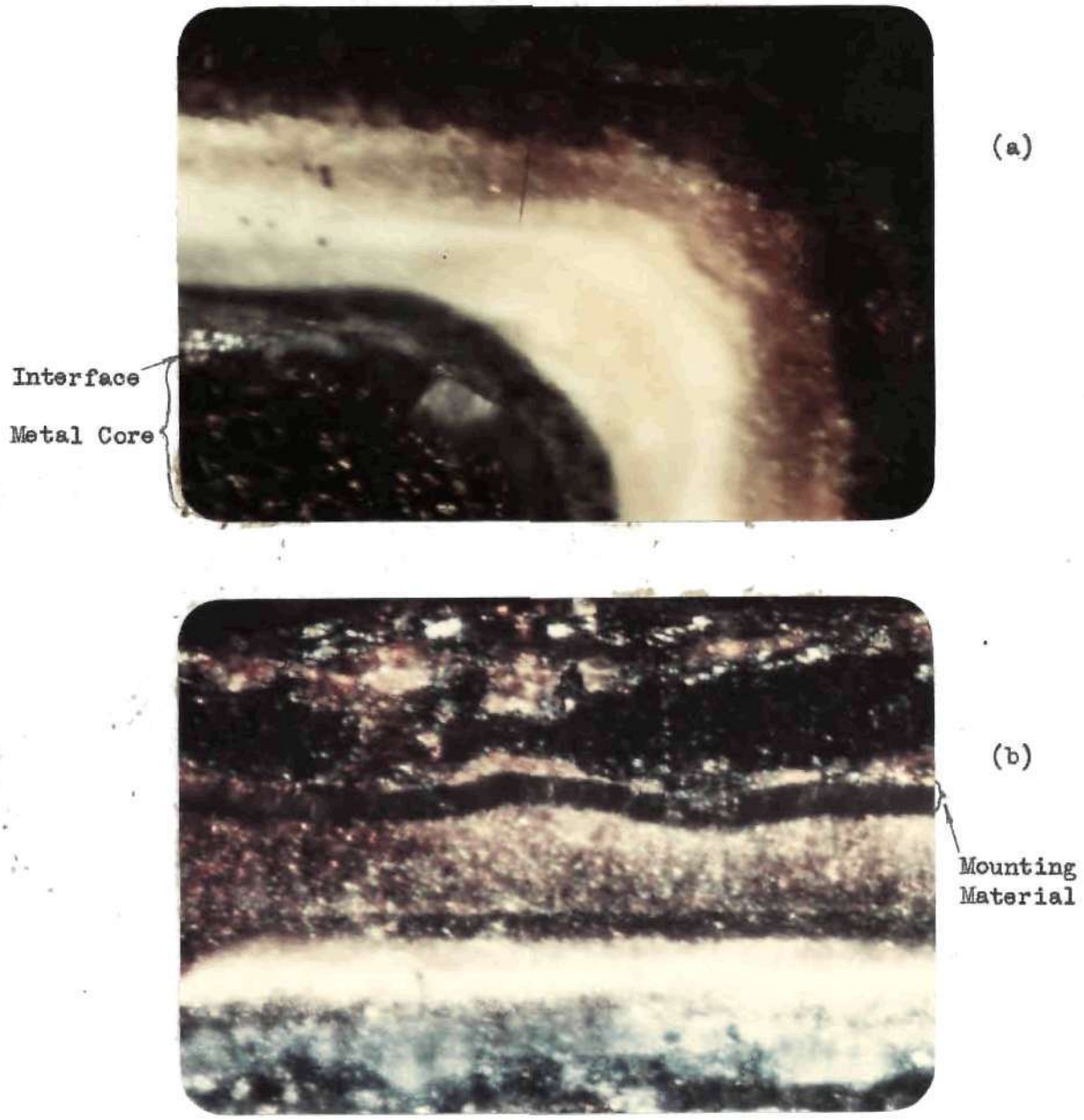


Figure 14. Kodachrome Micrographs. Shown above are micrographs of oxides grown for 20 hours at 950°C. on alloys (a) MST 2Al-2Fe and (b) MST 2.5Fe-2.5V. The lower edges were adjacent to the metal core. These micrographs are very good color reproductions. X86 and enlarged three times.

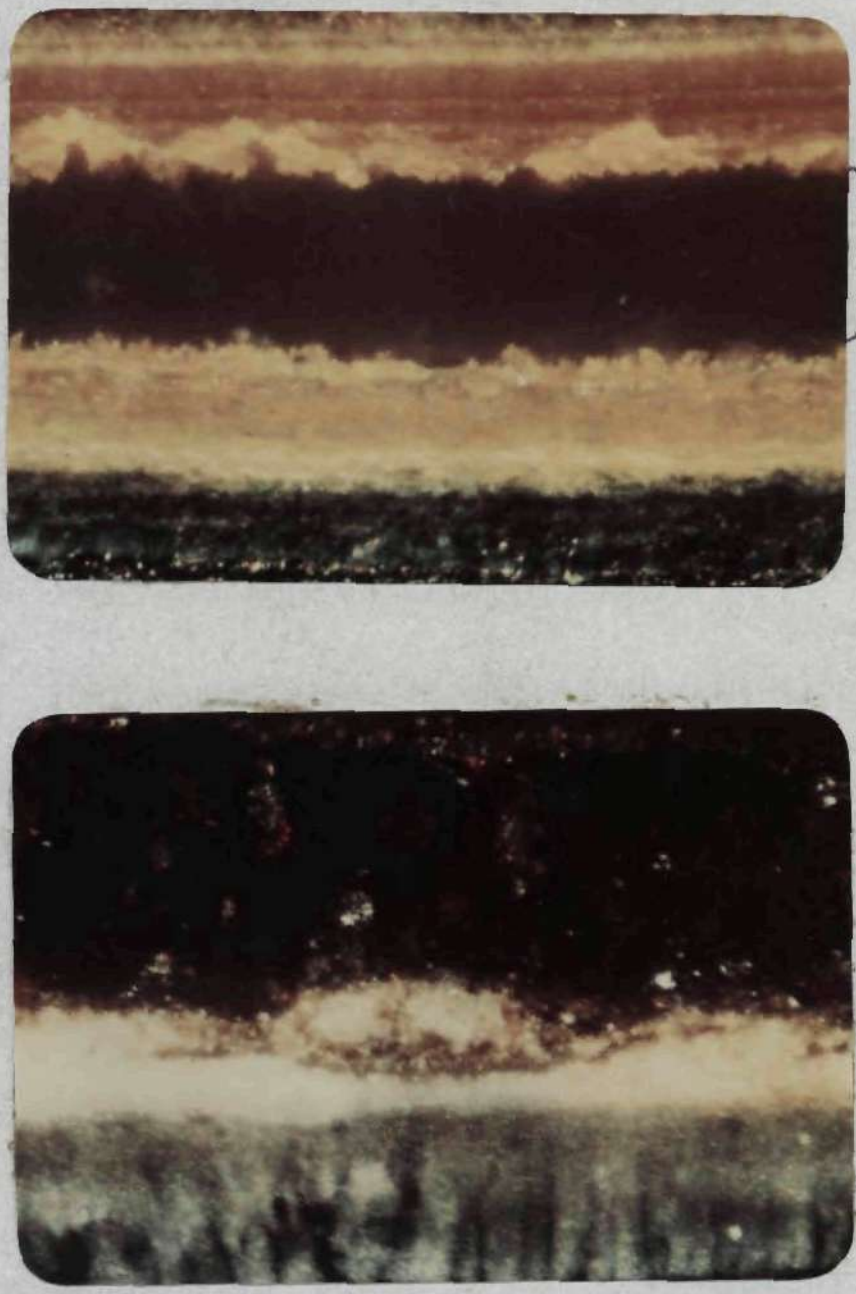


Figure 15. Kodachrome Micrographs. Shown in these micrographs are very good color reproductions of the oxides grown at 950°C. for 20 hours on (a) MST 3Al-5Cr and for 15 hours on (b) MST 2.5Fe-2.5V. The lower edges represent the section of the oxide that was adjacent to the metal core. The long striae or streaks in the oxide from MST 2.5Fe-2.5V were projections from the grain boundaries between dendrites in the core structure. 86X

Slate-gray. The correspondence between visual and polarization colors are given in Table 3.

All slate-gray oxides were found to be extremely brittle, hard and strong. Brown and yellow scales were friable and weak. Bright-yellow, white, charcoal, and gray oxides consisted of particles that possessed little or no strength.

The thin tenacious and continuous films exhibited Newton's interference colors in all cases.

Blisters, Strata and Outer Layers

The presence of blisters, strata and outer layers (or loose scales) at 950°C. and the absence of these phenomena at 700°C. can be explained. The explanation is based upon a consideration of the rate of oxidation relative to the rate of sintering.

Presence at 950°C.--The blisters, which resulted from oxidation at 950°C., were sections of sintered particles that have become highly stressed. Blister formation or mechanical breakdown was necessary to relieve the stresses developed during growth of the oxide.

These blisters grew in size and number until they formed one single continuous layer or scale which was nonadherent or only loosely adherent to the titanium metal. Immediately after the formation of a nonadherent layer, another layer began to form.

These layers, after separation from the metal core, reunited. However, the reunion was not complete and the result was the strata shown in Figures 8, 13, 14 and 15. The junctions between the layers, which caused the appearance of strata, were not well consolidated for two reasons. First, the time for sintering at the junctions was not as long

TABLE 3

CORRELATION OF COLORS OBSERVED
UNDER PLANE POLARIZED AND NATURAL LIGHT

POLARIZED	VISUAL
Blue-white Gray	Charcoal
Light yellow	Gray White
Light yellow	Bright yellow
Orange	Yellow Brown
Red Blue to dark blue	Slate gray

as the time for sintering within the layers; second, the contact pressure between the layers may not have been sufficient to promote good sintering. In time, however, the junctions with their resulting strata were erased by sintering.

Jenkins (11) attempted to explain scale formation as an occurrence that came about " ... when the thin, dense scale grew beyond a certain maximum thickness." The thin dense scale he refers to is a "...thin, dense, slate gray scale formed at low temperatures is replaced at high temperatures by a thick, porous, yellow-brown scale." He felt that the dense slate gray film occurred as a result of stress-free film growth and not as a result of highly stressed film growth that produced small particles which sintered together to form the slate gray oxide. In reality, the slate gray film replaced the yellow-brown oxide and not vice versa as Jenkins states it.

Absence at 700°C.--The absence of blisters, strata and outer layers or scales in the oxides formed at 700°C. (these oxides were always tenaciously adherent to the core metal) was a result of a faster oxidation rate relative to the sintering rate. This means that the stresses necessary to cause blister formation did not develop. Instead, slower sintering rates resulted in smaller forces and a more adherent oxide mass.

The relative rates of sintering at 700°C. and 950°C. may be determined by comparing the time required to obtain a given polarization color, since the oxide color is a function of the degree of sintering and, therefore, the oxide strength (i.e. the hardness, rigidity, stiffness and cohesion of the oxide). The relative rates of oxidation may be determined by comparing the oxide thickness. To show that the rate of oxidation

relative to sintering is lower with temperature, consider alloy MST 111. The oxide strength and the degree of sintering which are equivalent to an orange polarization color was first observed at an oxidation rate that corresponded to an oxide that was 0.002 inches thick at 950°C. and 0.001 inches thick at 700°C. Likewise, for alloy MST 3Al-5Cr, -- the oxide strength and the degree of sintering corresponding to a polarization color of yellow occurred at an oxidation rate equivalent to an oxide that was less than 0.001 inches thick at 950°C. and 0.001 inches thick at 750°C. These examples and others that are not stated here show, obviously, that the rate of oxidation relative to the sintering rate becomes smaller. This relative change may be stated another way: the rate of self diffusion of titanium dioxide is lower relative to the rate of diffusion of oxygen in titanium dioxide.

This change of the sintering rate relative to the oxidation rate was sufficient to cause a lowering of the stresses developed in the oxides at the lower temperature. By reason of this lowering, the oxides at 700°C. did not break down mechanically, whereas, the oxides at 950°C. blistered and formed outer layers or scales.

Visible Structure

The structures which were visible in the oxides are a reproduction of the structure present in the metal core.

Visible grains--Grain structures, which showed grain luster phenomena, were visible to the naked eye in the oxides formed during the early stages of oxidation at 950°C. These visible structures are a manifestation of vacuum macroetching which occurs in titanium by selective evaporation under vacuum of the metal from the various grains according to their

orientation. The oxides formed during the early stages of oxidation were simply too thin to obscure the undulations resulting from the macroetched surface; thus, the grain structures were visible. Figure 16 presents a micrograph showing an example of a visible oxide structure.

The presence of the visible grain structures is explained schematically in Figure 17.

The relation between the core structure and the film structure was confirmed experimentally. Long pieces of the titanium alloys were placed in the furnace so that they occupied zones of steep temperature gradients (these zones were excluded from normal experimental oxidation). The temperature gradients produced corresponding grain size gradients in the subsequent oxide. An edge of the oxidized sample was polished and given a macroetch. The polished metal had a grain size gradient that corresponded to the grain size gradient in the oxide. Furthermore, the grain boundaries, when compared at the edge where the oxide and the etched metal surface met, were seen to coincide. The hypothesis, consequently, that the visible grain structure in the oxide was a manifestation of the grain structure of the core was established.

The visible structures were eventually destroyed by sintering and the growth of thicker oxides.

Inhomogenities--Figure 18 pictures for comparison an unoxidized sample, macroetched, and an oxidized sample of titanium. These pictures show that the inhomogenious structure of the metal is reproduced in the oxide scale. Since both the oxide scale and the metal core displayed grain luster phenomena and since grain luster phenomena is dependent upon an undulated surface, the reproduction in the oxide is due to an uneven surface. These

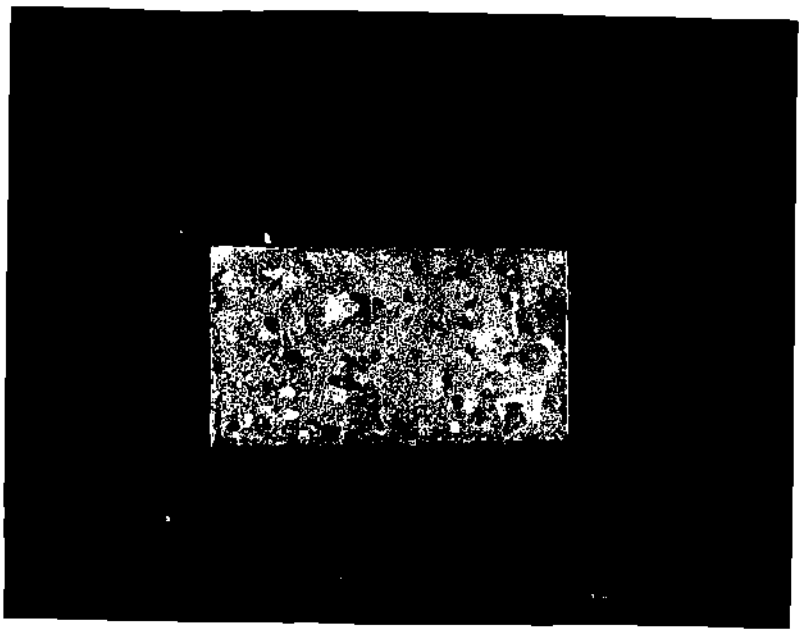


Figure 16. Visible Grain Structure. The picture shows the visible grain luster in the oxide from alloy MST 2Al-2Fe at 950°C. for three minutes. X4.

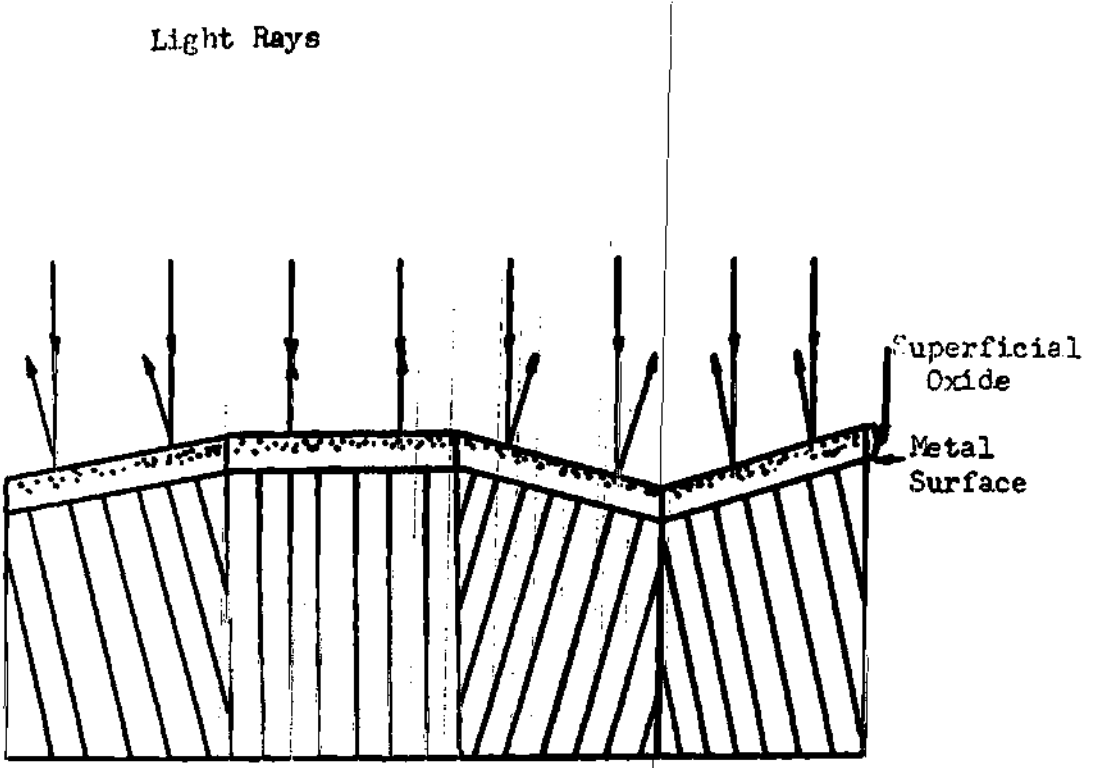


Figure 17. Model of Oxide Grain Luster Phenomena. The model shows how the structure of the metal surface, which was delineated by vacuum etching, can be reproduced by the oxide film formed on the metal's surface.

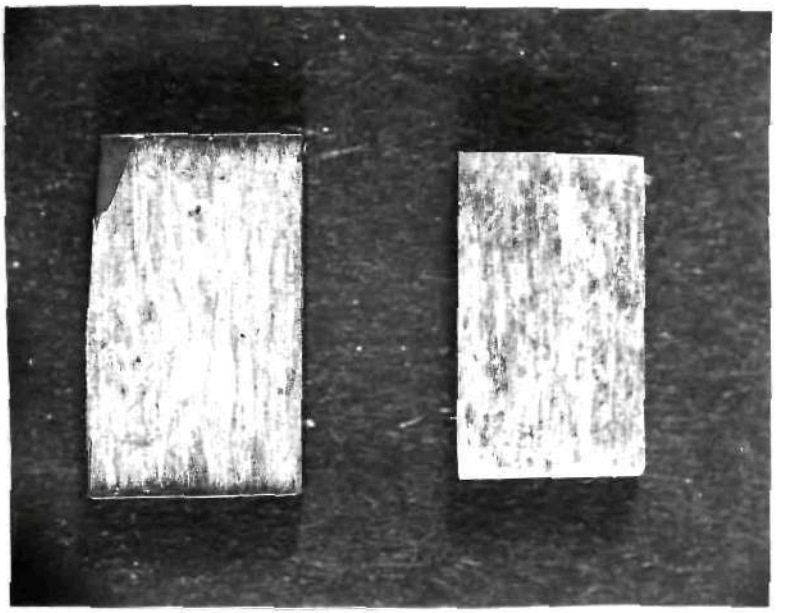


Figure 18. Metal Structure Reproduction in Oxide. The micrograph shows for comparison the metal structure (macroetched) and the same structure reproduced in the oxide which was grown for 170 hours at 700°C. on alloy RC130A. X4.

surface undulations in the oxide scale are the same undulations produced in the metal by vacuum etching prior to oxidation. The result is the reproduction of the inhomogeneous metal structure in the oxide. This structure, which is visible in the oxides grown up to 170 hours at 700°C., is another indication that the sintering at 700°C. does not cause violent upheavals in the oxide with the resulting erasure of the structure; that is to say, the violent upheavals resulting from stress relief by blister formation and mechanical breakdown do not accompany particle formation and sintering at 700°C. to obliterate the structure indicating undulations.

Stripped Films

To study the oxide surface present at, and adjacent to, the oxide metal interface, the oxide films were stripped from the metal and the "undersurface" examined. The structure, the reaction to polarized light, the formation of small particles and the overlapping grains in the thin, continuous, stripped films will now be discussed.

Structure--A typical micrograph of the stripped oxides formed in the early stages of oxidation on alloy MST 111 is pictured in Figure 19. The small grain structure in the large grains marked two and six deserve special consideration. The shapes of these small grains can be described appropriately as rectangular and lenticular laminae. These same structural shapes were present in some grains in the titanium samples which were vacuum etched in the beta region - above 950°C. The vacuum etch occurring as it does in the beta region, records the beta structure. See Figure 20. Bennet (3) has also published exceptional micrographs of these structures. The interested reader should refer to these.

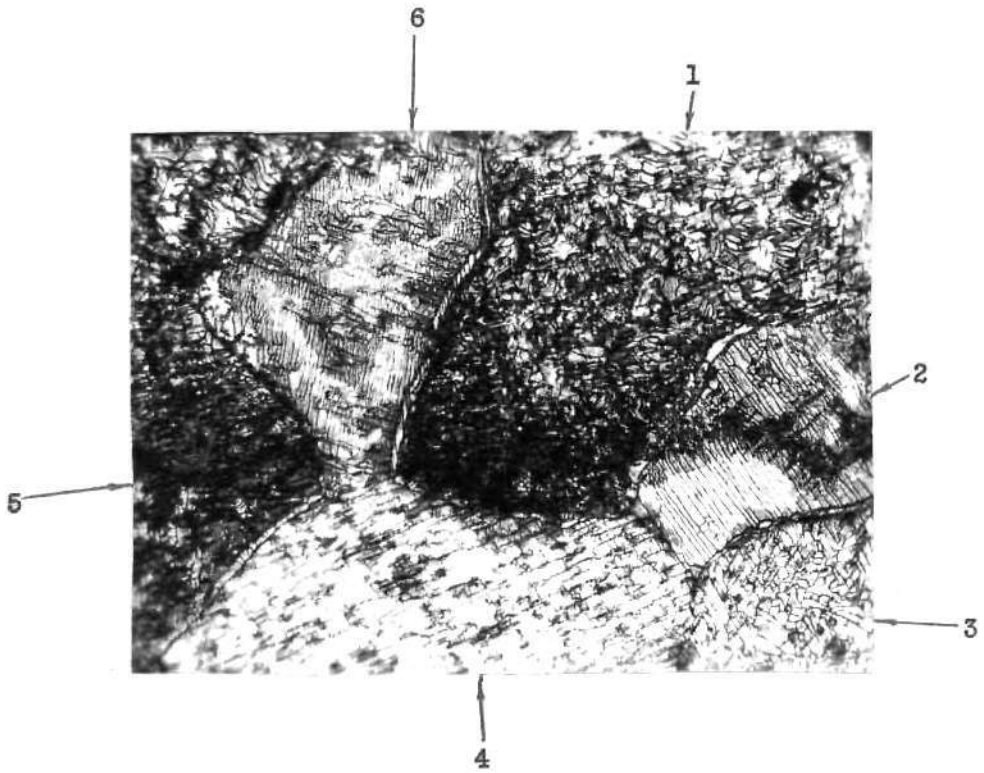


Figure 19. Lenticular Structure of Stripped Oxide. The picture shows a stripped oxide grown for three minutes at 950°C. on alloy MST 111. The lenticular and rectangular laminae shown in the grains marked two and six are identical in structure to similar grains that appeared in the metal core. Although the other large grains marked one, three, four, and five are reproductions of core structure, the small grains occurring in them are a result of recrystallization to relieve growth stresses. X250.

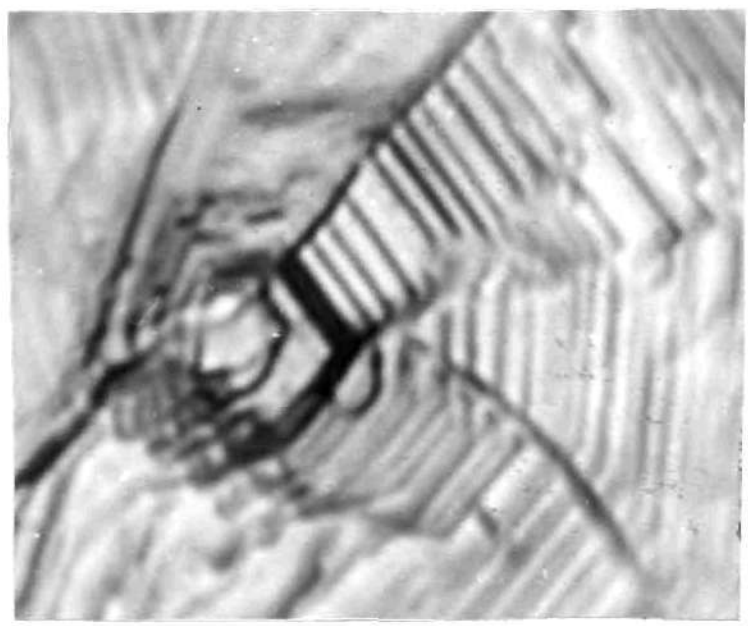


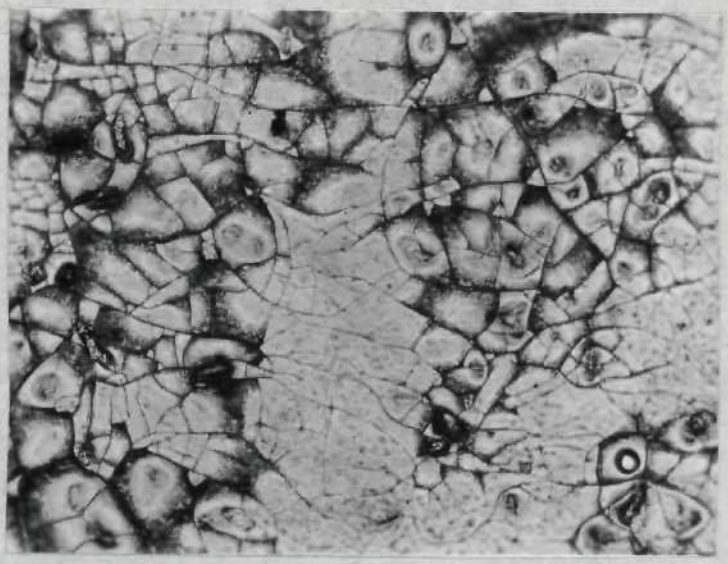
Figure 20. Rectangular and Lenticular Grains in Titanium. The micrograph reveals the vacuum etched structure which occurs in alloy MST 111. X1000 and enlarged three times.

These lenticular and rectangular striations are formed, according to Bennet, during the transformation from alpha to beta. He further asserts that the laminae are formed parallel to common planes of the two structures. This, Bennet explains, is why some grains - those with their common planes projecting in an unfavorable direction - did not display striations.

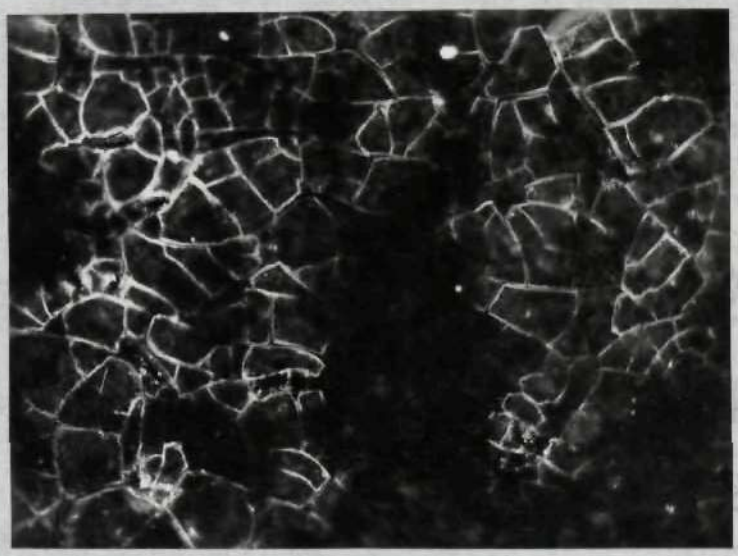
The occurrences of these lenticular grains in the structure of the oxide film demonstrates conclusively that the structure of the core metal is reproduced in the surface oxide. The oxide crystals, which precipitate from the core metal at nucleus points near the metal surface grow obviously by adding to their vacant lattice points, and, thus, propagate their structure in a direction parallel to the metal surface. Where two or more nuclei form within one grain of the metal structure, they will eventually unite since they possess the same crystalline structure and since they possess identical orientation because they form from the same crystal. After precipitation the oxide growth continues until the grain boundaries of the core metal prevent further growth. Thus the structure of the core metal is reproduced.

The large grains marked one, three, four, and five in Figure 18 are representative of the unfavorable oriented crystals where lenticular and rectangular grains did not form. The smaller grains in these large grains have formed by recrystallization to relieve stresses in the oxide.

Small particles--Figure 21 shows the formation of some small particles in the grain boundaries of the film structure. Recrystallization in the grain boundary areas is another typical result of stress relief.



(a)



(b)

Figure 21. Incipient Particle Formation in Grain Boundaries of Stripped Oxide. The picture shows the irregular grains with both sharp and diffuse grain boundaries of a stripped oxide grown for one minute on alloy RC130A at 950°C. Also shown are the particles in their early stages of formation. The lower micrograph (b) shows the appearance of the stripped oxide under polarized light. X250, grain size - 6/1047.

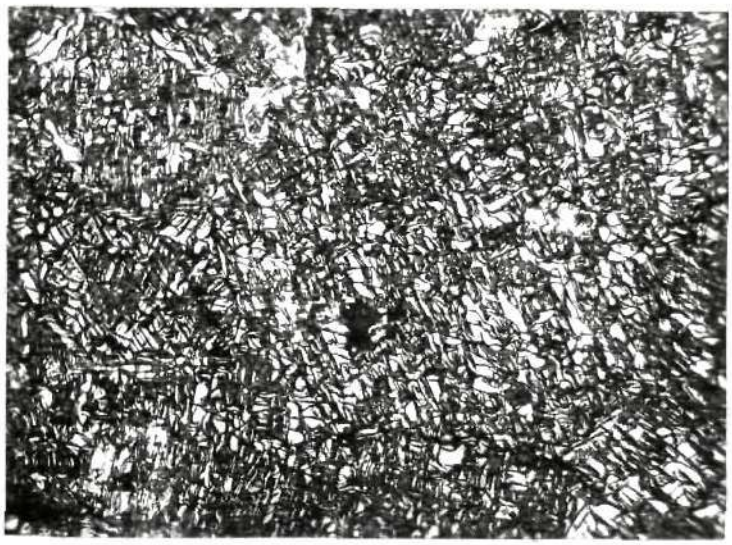
Typical oxide structures--Typical structures of the thin oxides are pictured in Figures 22 and 23. These pictures are representative of the thin films from all alloys with the exception of the thin, just-discussed, films grown during the early stages of oxidation at 950°C. on alloys RC130A and MST 111; investigation of the initial stages of oxidation would probably show identical structures in all alloys. The presence of these typical structures indicates that the films are stressed.

Overlapping grains--Overlapping grains possessed two structures: (1) a thin transparent layer of crystals over a second layer of crystals which possessed a structure similar to the first layer, and (2) a thin transparent layer of crystals over small porous particles.

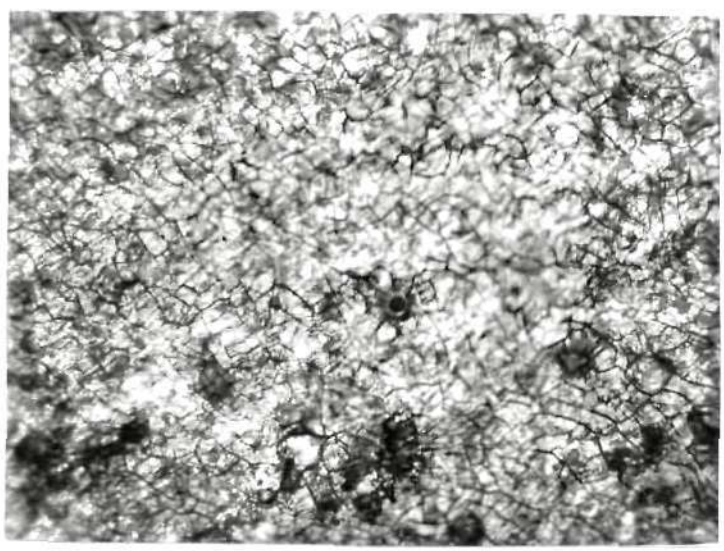
Observations under polarized light of the thin layer over the porous mass was difficult. The strong colored reaction of the small particles obliterated the detail and any possible polarized reaction that may have been present in the first layer of crystals.

A layer of crystals over a second layer of crystals was present only in the oxides stripped from alloy MST 111. The grains or crystals of the second layer, as reproduced in Figure 24, are outlined by their black and white reaction to polarized light. Some of the grain boundaries in the first layer can be seen in Figure 24 crisscrossing the grains of the second layer.

Polarized Light--Small sections of the thin films formed on alloy MST 111 and RC130A gave black and white reactions to polarized light. This phenomena was not observed in any oxides from the other alloys. The under layer of small particles, present in all cases on the other alloys and on alloys MST 111 and RC130A when the polarized reaction, if any, could



(a)



(b)

Figure 22. Typical Stripped Oxide Structure. Typical oxide structures from (a) alloy MST 111 for eight minutes at 950°C. and (b) alloy MST 3Al-5Cr for one minute at 950°C. are shown. (a) X250 grain size - 7/407 and (b) X500 grain size - 8/407

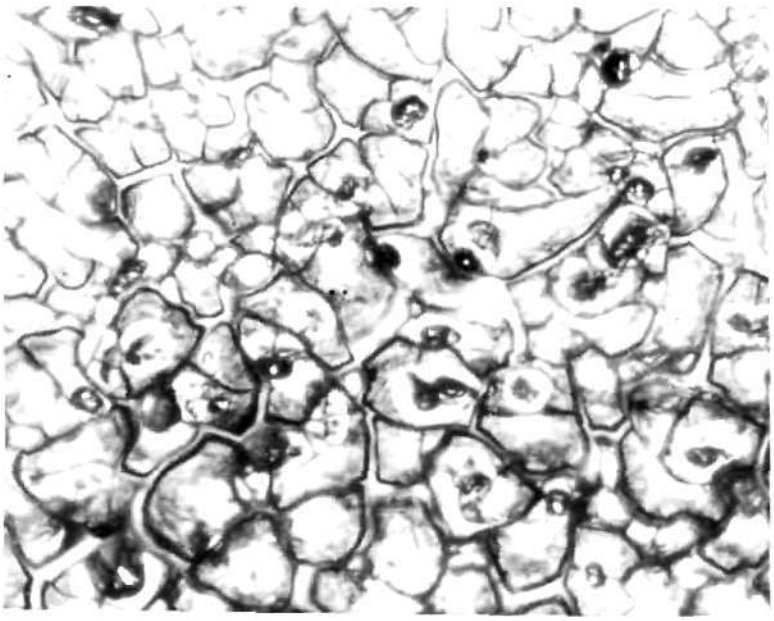


Figure 23. Diffuse Grain Boundaries in Structure of Stripped Oxide. The picture shows the structure of an oxide stripped from alloy RC130A grown for three minutes at 950°C. The diffuse grain boundaries probably represent recrystallized grains which are growing in the host structure but have not united. However, this structure may be another manifestation of overlapping grains. Notice what appears to be particle formation in some of these boundaries. X250 and enlarged two times.

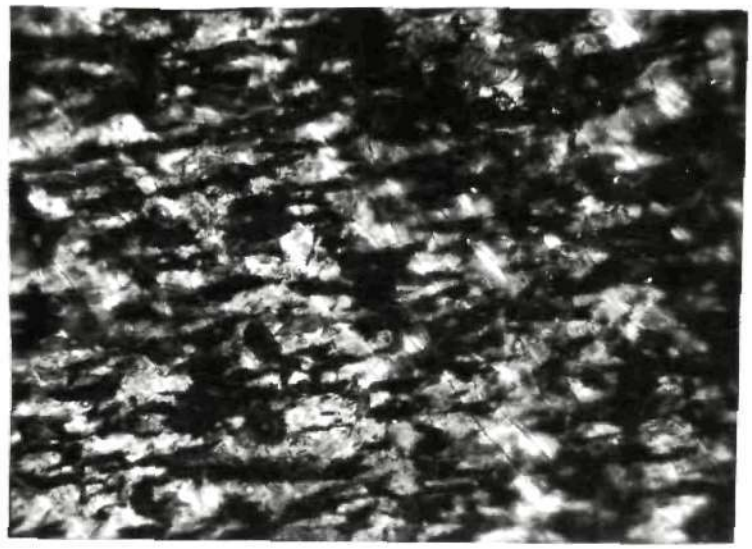


Figure 24. Overlapping Grain Structure in Stripped Oxide from Alloy MST 111. Overlapping grains are shown in the oxide grown for one minute at 950°C. The black and white grains in the second layer are outlined, partially, by their reaction to polarized light. Across these grains can be seen the grain boundaries of the grains in the first layer. X1000.

not be ascertained, gave such a strong colored reaction to polarized light that any possible reaction by the thin stripped films to polarized light could easily have been obscured. There is no evidence to indicate that a thorough investigation of the initial stages of oxidation would not show polarized reactions in all of the films.

Crystalline Structure of Oxide

Titanium dioxide was the only oxide product detected by X-ray diffraction studies on all of the alloys used in this study. This conformed to results obtained by other researchers (5, 8 and 11). However, the presence of only TiO_2 is in contradiction with the work of Richardson and Grant (16) who determined by extensive studies that TiO was present. Titanium oxide is also known (4) to give a strong reaction to polarized light. In view of these two facts, the presence of TiO is strongly suggested since small segments of the superficial oxides formed during the initial stages of oxidation gave definite reactions to polarized light.

The presence of TiO was indicated only in the early stages of oxidation at the metal-oxide interface of two alloys -- MST 111 and RC130A. Two of the stripped oxides, which were suspected of possessing some TiO, formed for one and three minutes at 950°C. on alloy MST 111 were subjected to glancing angle X-ray diffraction. None the less, the diffraction pattern indicated that only rutile was present. Evidently, the suspected TiO segments were present in quantities too small to be detected.

The absence of TiO during the later stages of oxidation is no doubt due to the high oxygen pressures used. The free energy data of Table 1 indicates that the equilibrium pressure between TiO and TiO_2 would be on

the order of 10^{-20} atmospheres. The pressure used in the present study during oxidation was one-tenth of an atmosphere. Since this is above the equilibrium pressure of TiO and TiO_2, the TiO phase is unstable.

Solution of Oxygen by Titanium

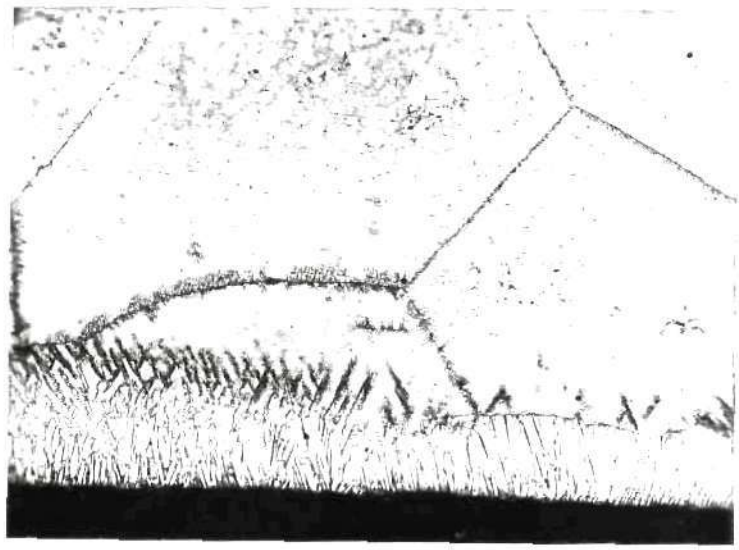
The various alpha formations and other experimental results show conclusively that the alloys used in this study dissolved oxygen. This conforms to results obtained by previous investigators (12 and 18) who have shown by chemical analysis that titanium dissolves oxygen.

Alpha formations--Various alpha dendritic formations are presented in Figures 25 and 26.

The alpha, which was formed at 950°C. from a beta structure, was precipitated by the solution of oxygen, an alpha stabilizer, in the beta.

The alpha dendrites shown in Figures 25 and 26 (a) are typical of structures formed by nucleation and phase growth in one direction. The mechanism is similar to dendritic formation in cast structures and is what would be expected by solution of oxygen, an alpha stabilizer, in the beta phase which was present at 950°C. Notice that the dendrites are parallel within a given grain. This implies, therefore, that the dendrites must be perpendicular to planes in the beta structure which offer a minimum interference and resistance to the diffusion of oxygen.

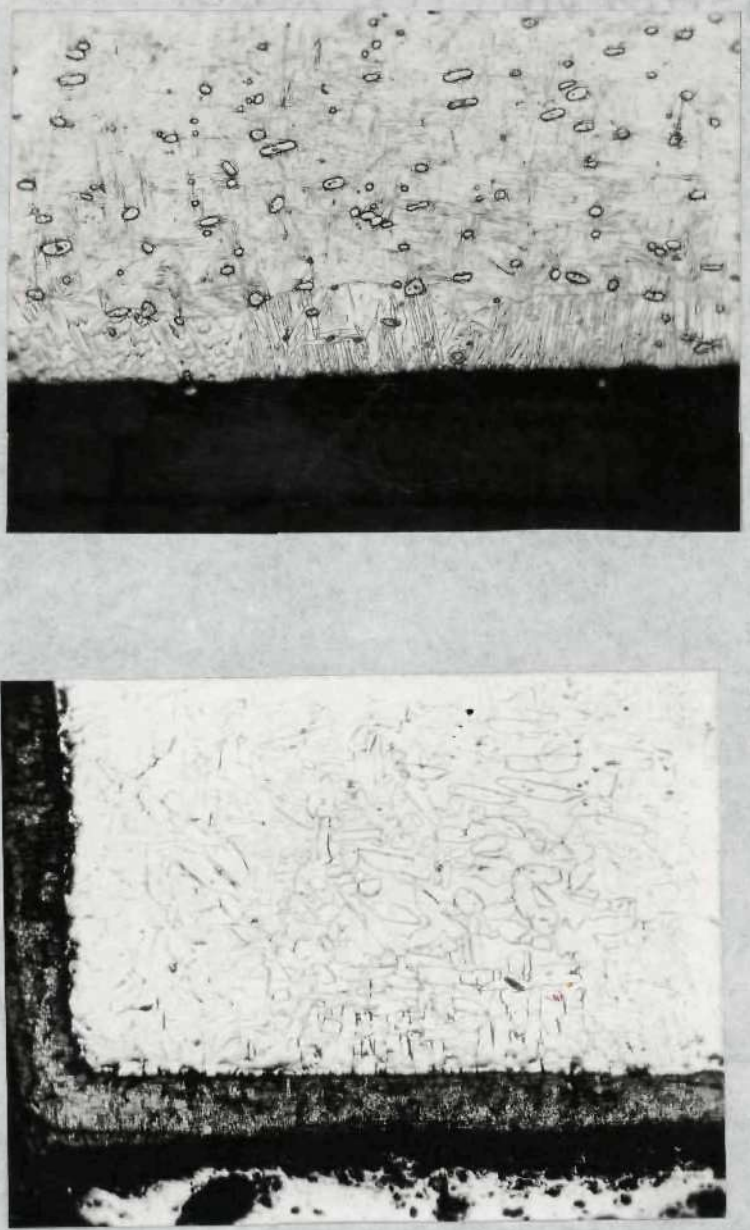
Figure 26 (b) displays for comparison a dendritic structure formed early in oxidation and the structure after considerable time has elapsed. The dendritic structure is more or less lost as a result of grain growth and extensive solution of oxygen and alpha formation.



(a)

(b)

Figure 25. Typical Dendritic Structures. (a) The Dendrites formed in alloys RC130A (a) and MST 111 (b) for 30 minutes and 30 seconds respectively at 950°C. The center section of alloy RC130A is composed of small precipitated alpha particles in the host beta structure. (a) X250; (b) X100.



(a)

(b)

Figure 26. Progress of Oxygen Solution. Alloy MST2.5Fe-2.5V is shown after oxidation for (a) 45 seconds and (b) 15 hours at 950°C. Continued oxygen solution in the metal eradicated the dendritic structure that forms early during oxidation at the metal surface (or edge) and the acicular transformation product of the metal core center. Due to the lower magnification, the titanium carbide particles are not readily discernable in the more oxidized structure. Notice the oxide film structure in the more oxidized structure. (a) X250 and (b) X98.

These Figures (25 and 26) show definitely that oxygen diffuses through any oxide barriers present on the surface and enters and diffuses into the titanium core.

Solution of oxygen may offer opportunities for surface hardening of titanium. Micro-hardness tests performed in the present study indicated as much. However, the tests were so sporadic that they were discontinued and the results are not reported.

Evidence of oxygen solution in titanium at 700°C. was sporadic, but layers of equiaxed alpha were thick enough to be observed in some instances. In general, the structure of the metal coarsened with time. This was probably due to grain growth as well as oxygen solution.

Solution of oxide scales--The oxides of titanium were dissolved by the metal core at 950°C. Titanium oxides, grown for two hours at 950°C., were left for two additional hours at 950°C. under a high vacuum in the vacuum furnace. The resulting samples were devoid of any superficial oxides, except some, very very few, charcoal specks. The structure of the resulting metal was essentially identical to the structure of the samples possessing superficial oxides.

Diffusion of oxygen--Prior to oxidation, small particles of inert kaolin were placed on the surface of the metal. The appearance of this kaolin on the subsequent oxide surface would demonstrate that the oxide grew under the kaolin by diffusion of oxygen into the titanium to form the oxide under the kaolin. However, the presence of the kaolin was difficult to determine and the results were doubtful. None the less, it was felt that kaolin was on the surface and that oxygen diffused into the titanium core.

Oxidation Rates

The oxidation rates reported by previous investigators (5, 7, 11, 16 and 18) lend themselves to interpretation by the results of this work.

During the early periods of oxidation, the thickness of the superficial oxide, which at this stage was thin and nonporous, was the only factor that affected the rate of oxidation or the rate of film growth. Since the rate of diffusion is proportional to the rate of film growth and inversely proportional to the film thickness, then the rate of film growth is inversely proportional to the film thickness. In mathematical terms this becomes

$$\text{diffusion rate} \propto \frac{d(\text{thickness})}{d(\text{time})} = \frac{k_1}{\text{thickness}}$$

$$\text{or} \quad (\text{thickness})^2 = k_1(\text{time}) \text{ plus } K_2$$

After a certain limiting film thickness is attained, the thickness is not a factor because the oxide becomes porous. Therefore, there should be two stages of oxidation: (1) A period of non-linear oxidation during which a thin film partially impervious to oxygen forms and grows; this film resists oxygen diffusion, and (2) A period of linear growth during which a thin film of a constant limited thickness controls the oxidation; thus the oxidation is linear. The main portion of the film during this period is porous and does not resist oxygen diffusion. There may be a third period in which the oxide scale loses its porosity because of extensive sintering. The present studies were not carried out for a sufficient length of time to study this aspect.

The non-linear oxidation rate in the initial stages of oxidation has been reported by several investigators. The rate of film growth during the early stage followed a modified parabolic rate law according to Gulbransen and Andrew. The modification no doubt is a result of the solution of oxygen in the metal core. Certainly, the diffusion rate of oxygen, as well as any element in the metal core, is dependent on the concentration gradient of the oxygen in the metal core. Also, as the initially oxygen free metal consumes more oxygen, the concentration gradient will be lowered and the diffusion rate will become slower. This premise was very recently authenticated by Sinnad, Spliners and Katz (18). They showed that the oxidation is slower but none the less linear on saturated titanium after the first two minutes. No doubt, the presence of TiO, if any, at the metal-oxide interface will also influence the initial rate of oxidation.

Jenkins (11) assumed the initial non-linear oxidation was due to establishing an oxygen concentration gradient in the core. He neglected the thin oxide barrier on the surface.

CHAPTER V

CONCLUSIONS

The following conclusions are a result of this investigation of the superficial oxides formed on some selected alloys of titanium at 700 and 950°C. in the presence of oxygen at one-tenth atmosphere pressure:

1. Titanium dioxide, as also shown by previous investigators, is the only superficial oxide detected by X-ray studies on the titanium alloys studied.

2. The superficial oxides of titanium undergo three distinct physical forms or stages of growth during the period when oxidation occurs: (1) Continuous tenacious film; (2) Small particles; and (3) Sintered particles.

3. The many colors exhibited by the superficial oxides of titanium, both when illuminated by fields of plane polarized and unpolarized light, were a function of the particles size of the oxides and, therefore, the degree of sintering and oxide strength.

4. The presence of blisters, strata, and loosely adherent scales in the oxides formed at 950°C. were the result of agglomerations of sintered particles breaking away from the core to relieve stresses which developed in the oxide.

5. The absence of blisters, strata, and loosely adherent scales in the oxides formed at 700°C. were due to a slow sintering rate, relative to the oxidation rate, which did not precipitate sufficient stresses to cause mechanical breakdown.

6. The visible structures present in the oxides were a reflection of vacuum etching of the titanium prior to oxidation.

7. The microstructure of the stripped oxides from alloys MST 111 and RC130A which were formed during the early, and only the early, stages of oxidation at 950°C. were proven to be identical to the microstructure of the core.

8. Segments of the stripped and unstripped oxide films from alloys MST 111 and RC130A at 950 and 700°C. formed during the early, and only the early, stages of oxidation gave a black and white reaction to polarized light; this reaction strongly indicates the presence of TiO at the metal-oxide interface.

9. The stripped oxide films possessed two types of overlapping layers that were discernible under a metallograph; (1) A thin transparent layer of nonporous and continuous crystals over a second layer of like structures and (2) A thin transparent layer of nonporous and continuous crystals over a second layer of small porous particles.

10. The oxide grows by the diffusion of oxygen through any impervious superficial oxide and into the titanium core.

11. The oxidation laws and their irregularities reported by previous investigators are explained on the basis of the three physical forms of the oxide that are formed during oxidation.

12. The superficial oxides from all the alloys appeared similar in all major points; in the cases where dissimilarity ostensibly appeared - polarized light reaction in the oxides from alloys MST 111 and RC130A at 950°C., overlapping crystals over similar crystals in the stripped oxides from alloy MST 111 at 950°C. and the reproduction of the core structure

in the stripped oxides from alloys MST 111 and RC130A at 950°C. -- there is no evidence to indicate that these differences would not be erased (the oxides would appear similar) by a more extensive study of the oxides formed during the initial oxidation periods.

CHAPTER VI

RECOMMENDATIONS

Evidence has been developed in the present investigation which shows fairly well the mechanism of oxide growth on titanium. An important aspect of oxide growth is the apparent formation of TiO at the metal-oxide interface during the early stages of oxidation on alloys RC130A and MST 111. Furthermore, in all cases where polarized light reaction was not observed - TiO apparently was not present - there was present under the thin continuous film of the stripped oxide a layer of small particles. Also, the evidence shows that the oxide structure during the early stages of oxidation is a reproduction of the structure in the metal core. These facts warrant a thorough investigation of the initial stages of oxidation which should encompass the following points: (1) A thorough study to show how the core structure is reproduced; (2) A study to determine definitely if TiO, and possibly other lower oxides, participate in any way during the formation of the dioxide; (3) A study to show if all the oxide films show polarized light reaction and if the absence in the cases noted in the present study is due to an overpowering reaction of small particles which may have obliterated the weaker reaction of the thin transparent films; and (4) A study to determine if there are any alloying elements that can prevent the solution of oxygen in titanium.

Experimental results developed in the present work show definitely that the particles present in the oxide scale sinter and, as a result, the scale becomes less porous. Studies to make use of and to develop a well sintered oxide that could be able of slowing the oxidation rate of titanium could advance the metal's technological status immensely.

APPENDIX

TABLE 4

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 111

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
30s			Single layer: tenacious, visible grain structure, dull gray	Edge: alpha dendrites, 0.001 inches; center: coarse acicular alpha in prior beta grains
45s	Light-Yellow		Outer layer: adherent, small particles that can be scraped off, dull gray with yellow cast, visible grain structure; core: tenacious, small particles, gold.	Edge: alpha dendrites, 0.001 inches; center: coarse acicular alpha in prior beta grains
1m	Light-Yellow		Outer layer: adherent, small particles that can be scraped off, dull gray with yellow cast; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.001 inches; center: coarse acicular alpha in prior beta grains
3m	Light-Yellow		Outer layer: adherent, some blisters present, rest small particles that can be scraped off, silver-gray; core: tenacious, small particles, gold and purple mixture	Edge: alpha dendrites, 0.002 inches; center: coarse acicular alpha in prior beta grains
5m	Light-Yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with slate-gray spots; core: tenacious, small particles, charcoal	Edge: alpha dendrites, 0.003 inches; center: coarse acicular alpha in prior beta grains

TABLE 4

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 111

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
8m	Orange, light-yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with evenly dispersed slate-gray spots; core: tenacious, small particles, charcoal	Edge: alpha dendrites, 0.003 inches; center: coarse acicular alpha in prior beta grains
30m	Orange, light-yellow, blue-white	0.002	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with evenly dispersed slate-gray spots; core: tenacious, small particles, charcoal	Edge: alpha dendrites, 0.005 inches; center: equiaxed alpha in matrix of coarse acicular alpha
2h	Orange, light-yellow, blue-white	0.002	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with evenly dispersed slate-gray spots; core: tenacious, small particles, charcoal	Edge: equiaxed alpha, 0.003 inches; alpha dendrites, 0.005; center: equiaxed alpha in matrix of coarse acicular alpha
5h	Orange, light-yellow, white, blue-white	0.002	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with evenly dispersed slate-gray spots; core: tenacious, small particles, charcoal	Edge: equiaxed alpha, 0.003 inches; center: equiaxed alpha in matrix of coarse acicular alpha

TABLE 4

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 111

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
9h	Red-orange, orange white, blue-white	0.003	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown and yellow mixture with evenly dispersed slate-gray spots; core: tenacious, small particles, charcoal	Edge: equiaxed alpha, 0.003 inches; center: equiaxed alpha in matrix of coarse acicular alpha
18h	Orange, gray, blue-white	0.004	Outer layer: non-adherent, brittle, fissures, sintering with voids and grain growth, surface: brown with purple cast and brown-yellow mixture, undersurface: loosely adherent particles, white; core: tenacious, small particles, charcoal	Edge: equiaxed alpha, 0.01 inches; center: equiaxed alpha in matrix of coarse acicular alpha
20h	Dark blue, white	0.008	Outer layer: non-adherent, brittle, fissures, sintering with voids and grain growth, surface: slate-gray, underside: loosely adherent particles, dark gray with green cast; core: tenacious, small particles, charcoal	Edge: equiaxed alpha, 0.006 inches; center: equiaxed alpha in matrix of coarse acicular alpha
20½	Blue, white	0.010	Outer layer: non-adherent, brittle, fissures, sintering with voids and grain growth, surface: slate-gray, underside: loosely adherent particles, blue-gray; core: tenacious small particles, charcoal	Edge: equiaxed alpha, 0.004 inches; center: equiaxed alpha in matrix of coarse acicular alpha

TABLE 5

OBSERVATIONS ON 950°C. STRIPPED OXIDES OF ALLOY MST 111

TIME	SIZE	SHAPE	COMMENTS	UNIFORMITY	TYPE MICROGRAPH
30s		Large irregular grains corresponding to metal structure; small grains within large grains: irregular, rectangular, lenticular, some small particles	Grains give black and white reaction to polarized light, small grains are oriented similar within large grains, small grain formation not complete in many of large grains	Non-uniform overall, but uniform within large grains	Sharp, but faint in some areas
45s		Large irregular grains corresponding to metal structure; small grains within large grains: irregular, rectangular, lenticular, some small particles	Grains give black and white reaction to polarized light, small grains are oriented within large grains, small grain formation not complete within many large grains	Non-uniform overall, but uniform within large grains	Sharp, but faint in some areas
1m		Large irregular grains corresponding to metal structure; small grains within large grains: irregular, rectangular, lenticular, some small particles	Some grains give black and white reaction to polarized light	Non-uniform overall, but uniform within large grains	Sharp, but faint in some areas, well developed overlapping grains
3m	7/407	Irregular, small particles	Small particles predominate	Fairly uniform	Diffuse
5m	7/407	Irregular, small particles	Mixture of areas containing small particles and grain structure	Fairly uniform	Diffuse
8m	7/407	Irregular, small particles	Area of grain structure predominates over area containing small particles	Fairly uniform	Diffuse

TABLE 5A

OBSERVATIONS ON 700°C. OXIDATION PRODUCTS OF ALLOY MST 111

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
10m			Single layer: tenacious, gives multicolored Newton's colors	No evidence of internal oxidation, the structure is essentially that of the unheated sample
30m			Single layer: tenacious, gives multicolored interference colors	No evidence of internal oxidation, the structure is essentially that of the unheated sample
1h			Single layer: tenacious, film has pink cast, small particles	No evidence of internal oxidation, the structure is essentially that of the unheated sample
4h	Light yellow		Single layer: tenacious, small particles, sintering and grain growth, gray	No evidence of internal oxidation, the structure is essentially that of the unheated sample
15h	Light yellow		Single layer: tenacious, small particles, sintering and grain growth, gray	No evidence of internal oxidation, the structure is essentially that of the unheated sample
30h	Light yellow, blue-white	0.001	Single layer: tenacious, small particles, sintering and grain growth, gray	No evidence of internal oxidation, the structure is essentially that of the unheated sample
170h	Light yellow, blue-white	0.003	Single layer: tenacious, small particles, sintering and grain growth	Layer of alpha, 0.005; sample center: alpha plus dispersed particles, alpha larger on edge

TABLE 6

OBSERVATIONS ON 700°C. STRIPPED OXIDES OF ALLOY MST 111

TIME	SIZE	SHAPE	EXAMINATION	UNIFORMITY	TYPE MICROGRAPH
30m	6/1047	Irregular	Polarized light: black and white reaction	Fairly uniform	Diffuse
10m	6/1047	Irregular	Polarized light: black and white reaction	Fairly uniform	Diffuse, undulated
1h	6/1047	Irregular	Polarized light: black and white reaction	Fairly uniform	Diffuse, undulated
4h	6/1047		Bright light: many small particles, particles appear gray under polarized light		
15h	6/1047	Irregular	Polarized light: gray reaction; bright light: many small particles beginning to form	Fairly uniform	Diffuse, overlapping
30h	6/1047	Irregular	80 per cent mixture of small particle and 20 per cent large grains, small particles appear gray under polarized light	Non-uniform	Diffuse, overlapping
60h	6/1047	Irregular	Large grains over small grains	Fairly uniform	Diffuse, overlapping

TABLE 7

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY RC130A

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
30s			Single layer: tenacious, visible grain structure, dull gray	Edge: alpha dendrites, 0.001 inches; center: traces of alpha in a beta matrix
45s	Light-yellow		Outer layer: adherent, small particles that can be scraped off, visible grains, dull gray with yellow cast; core, small particles, gold	Edge: alpha dendrites, 0.001 inches; center: traces of alpha in a beta matrix
1m	Light-yellow	0.001	Outer layer: adherent, small particles that can be scraped off, slightly visible grain structure, dull gray with brown cast; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.001 inches; center: traces of alpha in a beta matrix
3m	Orange, light-yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, silver-gray with blue cast; core: tenacious, small particles, gold and blue mixture	Edge: alpha dendrites, 0.002 inches; center: traces of alpha in a beta matrix
5m	Orange, light-yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown; core: tenacious, small particles, blue and purple mixture	Edge: alpha dendrites, 0.002 inches; center: traces of alpha in a beta matrix

TABLE 7

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY RC130A

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
8m	Orange, light-yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown; core: tenacious, small particles, gold and blue mixture	Edge: alpha dendrites, 0.003 inches; center: traces of alpha in a beta matrix
12m	Orange, light-yellow	0.001	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown; core: tenacious, small particles, gold and blue mixture	Edge: alpha dendrites, 0.004 inches; center: traces of alpha in a beta matrix
30m	Orange, light-yellow, white	0.002	Outer layer: loosely adherent, friable, fissures, sintering with voids and grain growth, brown; core: tenacious, small particles, gold and blue mixture	Edge: alpha dendrites, 0.006 inches; center: traces of alpha in a beta matrix
2h	Orange, light-yellow, white	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, dark brown and purple cast, underside: loosely adherent small particles, white; core: tenacious, small particles, charcoal with some white particles	Edge: alpha dendrites, 0.014 inches; center: traces of alpha in a beta matrix
5h	Red-orange, orange, white, blue-white	0.003	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast, underside: loosely adherent small particles, white; core: tenacious; small particles, charcoal with some white	Edge: alpha dendrites, 0.017 inches; center: traces of alpha in a beta matrix

TABLE 7

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY RC130A

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
9h	Orange, white	0.004	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, visible grain structure, surface: dark brown with purple cast, underside: small loose particles, white; core: tenacious, small particles, charcoal with some white	Edge: alpha dendrites extending across sample in a beta matrix
18h	Blue, light orange, gray with darker shoots that correspond to the grain boundaries	0.011	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast, underside: small loose particles, white; core: tenacious, small particles, charcoal with some white	Alpha dendrites extending across sample in a beta matrix containing traces of alpha
20h	Dark blue, light blue and white mixture, layers of light blue and white, dark shoots corresponding to grain boundaries	0.016	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: slate-gray, blue-gray, underside: small loose particles, white; core: tenacious, small particles, charcoal with some white	Alpha dendrites extending across sample in a beta matrix containing traces of alpha
21½	Dark blue, light blue, white, gray	0.006	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: slate-gray, underside: blue-gray; core: tenacious, small particles, charcoal with some white	Alpha dendrites extending across sample in a beta matrix containing traces of alpha

TABLE 8

OBSERVATIONS ON 950°C. STRIPPED OXIDES OF ALLOY RC130A

TIME	SIZE	SHAPE	COMMENTS	UNIFORMITY	TYPE MICROGRAPH
30s	7/407	Irregular	Appears gray under polarized light, rainbows at grain boundaries, about half of area without developed grain structure, black and white reaction to polarized light	Non-uniform	Sharp, overlapping
45s	7/407	Irregular particles	Gray under polarized light, grain boundaries appear white, about 5 per cent small particles, small particles appear white under polarized light	Fairly uniform	Medium sharp, overlapping
1m	8/407	Irregular, small	Yellow under polarized light, grain boundaries appear white	Fairly uniform	Diffuse and sharp mixture overlapping
8m	7/407	Irregular	Gray under polarized light, small particles appear white, about half are small particles	Fairly uniform	Diffuse, overlapping

TABLE 9

OBSERVATIONS ON 700°C. OXIDATION PRODUCTS OF ALLOY RC130A

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
10m			Single layer: tenacious, metal's inhomogenity shown in film, silver gray	No evidence of internal elongated oxidation, small alpha grains in a beta matrix, similar to un-oxidized sample
30m			Single layer: tenacious, metal's inhomogenity shown in film, silver gray	No evidence of internal elongated oxidation, small alpha grains in a beta matrix, similar to un-oxidized sample
1h	Light-yellow	0.001	Single layer: tenacious, metal's inhomogenity shown in film, small particles, dull gray	No evidence of internal oxidation, small alpha grains in beta matrix, similar to unoxidized sample (coarsening and annealing)
4h	Light-yellow	0.001	Single layer: tenacious, metal's inhomogenity shown in film, small particles, dull gray	No evidence of internal oxidation, small alpha grains in beta matrix, similar to unoxidized sample (coarsening and annealing)
15h	Orange, light-yellow	0.001	Single layer: tenacious, metal's inhomogenity shows in film, small particles, sintering with voids and grain growth, slate-gray and brown mixture	Some increase in quantity of alpha phase at edge, small alpha grains in beta matrix — similar to unoxidized sample
30h	Orange, light-yellow	0.001	Single layer: tenacious, gray and brown mixture, inhomogenity of metal sample shows in film, sintering with grain growth, slate-gray and brown mixture	Sample edge: quantity of alpha in beta greater at edge; sample center: alpha in beta matrix

TABLE 9

OBSERVATIONS ON 700°C. OXIDATION PRODUCTS OF ALLOY RC130A

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
60h	Red, orange, light-yellow	0.002	Single layer: tenacious, slate-gray and brown mixture, inhomogenity of metal sample shows in film, small particles, sintering with voids and grain growth	Sample edge: quantity of alpha in beta matrix, quantity of alpha greater at edge
170h	Red, orange, light-yellow	0.003	Single layer: tenacious, inhomogenity of metal shown in most sections of film, small particles, sintering with grain growth, slate-gray	Sample edge: beta in alpha matrix; sample center: alpha in beta matrix

TABLE 9A

OBSERVATIONS ON 700°C. STRIPPED OXIDES OF ALLOY RC130A

TIME	SIZE	SHAPE	EXAMINATION	UNIFORMITY	TYPE MICROGRAPH
10m	6/1047	Irregular	Many small particles present that appear yellow under polarized light	Non-uniform	Diffuse
30m	6/1047	Irregular, angular	Most of film composed of small particles which appear yellow and gray under polarized light	Non-uniform	Diffuse, overlapping
15h	6/1047	Irregular, angular	Polarized light necessary to bring out grain boundaries which appear white, 80 per cent small particles which appear yellow under polarized light	Fairly uniform	Diffuse, overlapping
60h	6/1047	Irregular, angular	Film gives a green-blue interference color, areas present that have small grains	Fairly uniform	Diffuse, overlapping

TABLE 10

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2.5Fe-2.5V

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
30s	Light-yellow		Single layer: tenacious, small particles, visible grain structure, dark blue with yellow cast	Edge: alpha dendrites, 0.001 inches; center: fine acicular transformation product in prior beta grains; evenly dispersed TiC throughout sample
45s	Orange, yellow		Outer layer: adherent, small particles that can be scraped off, visible grain structure, brown; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.001 inches; center: fine acicular transformation product in prior beta grains; evenly dispersed TiC particles throughout sample
1m	Orange, yellow	0.001	Outer layer: adherent, small particles that can be scraped off, brown; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.002 inches; center: fine acicular transformation product in prior beta grains, evenly dispersed TiC particles throughout sample
3m	Orange, yellow	0.001	Outer layer: adherent, small particles that can be scraped off, brown; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.002 inches; center: fine acicular transformation product in prior beta grains; evenly dispersed TiC particles throughout sample
5m	Orange, yellow	0.001	Outer layer: adherent, small particles that can be scraped off, blisters, brown; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.002 inches; center: fine acicular transformation product in prior beta grains, evenly dispersed TiC particles

TABLE 10

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2.5Fe-2.5V

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
8m	Orange, yellow	0.001	Outer layer: adherent, small particles that can be scraped off, blisters, brown; core: tenacious, small particles, gold and purple mixture	Edge: alpha dendrites, 0.002 inches; center: fine acicular transformation product in prior beta grains, evenly dispersed TiC particles
12m	Orange, yellow	0.001	Outer layer: nonadherent, friable, sintering with voids and grain growth, brown; core: tenacious, small particles, gold and purple mixture	Edge: alpha dendrites, 0.003 inches; center: fine acicular transformation in prior beta grains; evenly dispersed TiC particles throughout sample
30m	Orange, yellow	0.001	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: brown, undersurface: small loose particles, white; core: tenacious, small particles, charcoal with some white	Edge: alpha dendrites, 0.004 inches; center: fine acicular transformation product in prior beta grains; evenly dispersed TiC particles throughout sample
2h	Deep orange, yellow, blue-white	0.002	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast and slate-gray mixture, undersurface: small loose particles, white, core: tenacious, small particles, charcoal with some white	Edge: alpha dendrites, 0.009 inches; center: fine acicular transformation product in prior beta grains; evenly dispersed TiC particles throughout sample

TABLE 10

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2.5Fe-2.5V

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
5h	Dark-red, orange, light yellow, blue-white	0.002	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast and slate-gray mixture, under-surface: small loose particles, white; core: tenacious, small particles, charcoal with some white	Alpha dendrites that extend across sample with matrix of fine acicular transformation product; evenly dispersed TiC particles throughout sample
9h	Dark-red and orange mixture, dull light-yellow, white	0.002	Outer surface: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast and slate-gray mixture, under-surface: small loose particles, white; core: tenacious, charcoal with some white	Alpha dendrites that extend across sample with matrix of fine acicular transformation product, evenly dispersed TiC particles throughout sample
15h	Dark-blue with touch of red, orange, gray with blue cast and darker shoots that correspond to grain boundaries	0.006	Outer surface: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast and slate-gray mixture, under-surface: small loose particles, white; core: tenacious, small particles, charcoal with some white	Alpha dendrites that extend across sample with matrix of fine acicular transformation product, evenly dispersed TiC particles throughout sample

TABLE 10

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2.5Fe-2.5V

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
18h	Dark-blue with touch of red, orange, gray with blue cast and darker shoots that correspond to grain boundaries	0.008	Outer surface: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast and slate-gray mixture, undersurface: small loose particles, white; core: tenacious, small particles, charcoal with some white	Alpha dendrites that extend into center of sample with matrix of fine acicular transformation product, evenly dispersed TiC particles throughout sample
20h	Dark-red, orange, white, blue-white with blue shoots that correspond to grain boundaries	0.010	Outer surface: nonadherent, brittle, sintering with voids and grain growth, surface: slate-gray, undersurface: small loose particles, gray with brown cast; core: tenacious, small particles, charcoal with some gray with brown cast	Alpha dendrites that extend across sample with a matrix of fine acicular transformation product, evenly dispersed TiC particles throughout sample
21½	Dark red, white, blue	0.002	Outer surface: nonadherent, brittle, sintering with voids and grain growth, surface: slate-gray, undersurface: small loose particles, gray with brown cast; core: tenacious, small particles, charcoal with some gray with brown cast	Alpha dendrites that extend across sample with a matrix of fine acicular transformation product, evenly dispersed TiC particles throughout sample

TABLE 11

OBSERVATIONS ON 950°C. STRIPPED OXIDES OF ALLOY MST 2.5Fe-2.5V

TIME	SIZE	SHAPE	COMMENTS	UNIFORMITY	TYPE MICROGRAPH
30s	8/407	Irregular, small particles	Gray under polarized light, grain boundaries appear white under polarized light, 10 per cent small particles appear white	Fairly uniform	Sharp
45s	8/407	Irregular	Gray under polarized light, no evidence of small particles	Fairly uniform	Sharp
1m	6/407	Irregular	Gray under polarized light, 10 per cent small particles appear white	Fairly uniform	Sharp
3m	6/407	Irregular	Gray under polarized light, 15 per cent small particles appear white under polarized light	Fairly uniform	Sharp
5m	6/407	Irregular	Gray under polarized light, 15 per cent small particles appear white under polarized light	Fairly uniform	Sharp, overlapping
8m	6/407	Irregular	Gray under polarized light, 20 per cent small particles appear white under polarized light	Fairly uniform	Sharp, overlapping
30m	6/407	Irregular	Gray under polarized light, 20 per cent small particles appear white under polarized light	Fairly uniform	Sharp, overlapping

TABLE 12

OBSERVATIONS OF 700°C. STRIPPED OXIDES OF ALLOY MST 2.5Fe-2.5V

TIME	SIZE	SHAPE	EXAMINATION	UNIFORMITY	TYPE MICROGRAPH
10m	6/1047	Very irregular	TiC gray particles present in film, polarized light makes grain boundaries white, grains appear gray under polarized light	Non-uniform	Diffuse, overlapping
30m	6/1047	Irregular	TiC particles present in film, grain boundaries appear white under polarized light, small particles appear dark gray and blue-white	Fairly uniform	Diffuse, overlapping
1h	6/1047	Irregular	Gray and blue-white TiC particles present in film, grain boundaries appear white under polarized light, many small grains present	Non-uniform	Medium sharp, faint, overlapping
4h	6/1047	Irregular, small particles	White and orange TiC particles present in film, grain boundaries appear white under polarized light, small particles appear white and orange	Fairly uniform	Medium sharp, overlapping
60h	6/1047	Irregular	Orange TiC particles present in film, grain boundaries appear white under polarized light, small particles appear orange	Fairly uniform	Diffuse, overlapping

TABLE 13

OBSERVATIONS OF 700°C. OXIDATION PRODUCTS OF ALLOY MST 2.5Fe-2.5V

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF METAL SAMPLE
10m	Light-yellow		Single layer: tenacious, small particles, metallic	No sign of internal oxidation, fine acicular transformation product, evenly dispersed TiC particles throughout sample
30m	Light-yellow		Single layer: tenacious, small particles, metallic	No sign of internal oxidation, fine acicular transformation product, evenly dispersed TiC particles throughout sample
1h	Light-yellow	0.001	Single layer: tenacious, small particles, dull metallic	No sign of internal oxidation, fine acicular transformation product, evenly dispersed TiC particles throughout sample
4h	Light-yellow	0.001	Single layer: small particles, tenacious, dull metallic	No sign of internal oxidation, fine acicular transformation product, evenly dispersed TiC particles throughout sample
15h	Light-yellow, blue-white	0.001	Single layer: tenacious, small particles, gray with brown cast	Coarsening acicular transformation product, evenly dispersed TiC particles throughout sample
30h	Orange, yellow, blue-white	0.001	Single layer: tenacious, small particles, brown	Coarsening acicular transformation product, evenly dispersed TiC particles throughout sample
60h	Orange, light-yellow	0.001	Single layer: tenacious, small particles, sintering with voids and grain growth, brown	Coarsening acicular transformation product, evenly dispersed TiC particles throughout sample
170h	Orange, light-yellow	0.002	Tenacious, small particles, sintering with voids and grain growth, dark brown	Sample edge: beta in alpha matrix; sample center: beta in alpha matrix (very coarse transformation product) evenly dispersed TiC particles throughout sample

TABLE 14

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 3Al-5Cr

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
30s	Yellow		Single layer: tenacious, small particles, blue and yellow mixture	Edge: alpha dendrites; center: fine acicular transformation product in prior beta grains equiaxed alpha in prior beta grain boundaries, dispersed TiC particles
45s	Yellow		Single layer: tenacious, small particles, blue and yellow mixture	Edge: alpha dendrites, 0.001 inches; center: fine acicular transformation product in prior beta grains, equiaxed alpha in prior beta grain boundaries, dispersed TiC particles
1m	Yellow	0.001	Single layer: adherent, small particles that can be scraped off, yellow elongated blisters parallel to inhomogenity marks, rest yellow and blue mixture; core: tenacious, small particles, gold and blue mixture	Edge: alpha dendrites, 0.001 inches; center: matrix of fine acicular transformation product in prior beta grains and equiaxed alpha in prior beta grain boundaries, dispersed TiC particles
3m	Yellow	0.001	Outer layer: loosely adherent, friable, small particles that can be scraped off, yellow; core: tenacious, small particles, gold	Edge: equiaxed alpha, 0.001 inches; center: equiaced alpha in matrix of fine acicular transformation product, dispersed TiC particles

TABLE 14

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 3Al-5Cr

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
8m	Orange, yellow	0.001	Outer layer: nonadherent, friable, fissures, sintering with voids and grain growth, surface: brown and yellow mixture with charcoal spots, undersurface: small loose particles, tan and yellow mixture; core: tenacious, small particles, gold	Edge: equiaxed alpha, 0.001 inches; center: equiaxed alpha in matrix of fine acicular transformation product in prior beta grains and equiaxed alpha in prior beta grain boundaries, dispersed TiC particles
30m	Orange, yellow	0.002	Outer layer: nonadherent, friable, fissures, sintering with voids and grain growth, surface: brown and yellow mixture with charcoal spots, undersurface: small loose particles, tan and yellow mixture; core: tenacious, small particles, brown and yellow and charcoal mixture	Edge: equiaxed alpha, 0.005 inches; center: equiaxed alpha in matrix of fine acicular transformation product in prior beta grains and equiaxed alpha in prior beta grain boundaries, dispersed TiC particles
2h	Orange, yellow	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: tan with charcoal spots, undersurface: small loose particles, tan and yellow mixture; core: tenacious, small particles, yellow and charcoal mixture	Edge: fine acicular transformation product in an alpha matrix, 0.001 inches; center: equiaxed alpha in matrix of fine acicular transformation product in prior beta grains and equiaxed alpha in prior beta grain boundaries, dispersed TiC particles

TABLE 14

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 3Al-5Cr

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
5h	Orange, yellow	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: tan with charcoal spots, undersurface: small loose particles, tan and yellow mixture; core: tenacious, small particles, yellow and charcoal mixture	Edge: fine acicular transformation product in an alpha matrix, 0.001 inches; center: equiaxed alpha in fine acicular transformation product
9h	Orange, yellow	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: brown with purple cast, core: small particles of tenacious charcoal covered with loosely adherent yellow particles	Edge: fine acicular transformation product in an alpha matrix, 0.001 inches; center: equiaxed alpha in fine acicular transformation product
15h	Orange, yellow	0.003	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast, undersurface: small loose particles, yellow; core: small particles of tenacious charcoal covered with loosely adherent yellow particles	Edge: fine acicular transformation product in an alpha matrix, 0.001 inches; center: equiaxed alpha in matrix of fine acicular transformation product
18h	White, orange, yellow, gray, blue with dark blue spots corresponding to transformation product	0.006	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast, underside: loosely adherent, small particles, yellow, core	Edge: fine acicular transformation product in a matrix of alpha, 0.003 inches; center: equiaxed alpha in matrix of fine acicular transformation product

TABLE 14

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 3Al-5Cr

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
20h	White-purple, orange, yellow, gray, blue with dark blue shoots that correspond to transformation product	0.007	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast, underside: small loosely adherent particles, yellow; core: small particles of tenacious charcoal covered with loosely adherent yellow particles	Edge: fine acicular transformation product in a matrix of alpha, 0.002 inches; center: equiaxed alpha in transformation matrix, dispersed TiC particles
20½	Dark red, yellow, gray with dark shoots, shoots correspond to transformation product	0.005	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: dark brown with purple cast and slate-gray mixture, underside: small particles of tenacious charcoal covered with loosely adherent yellow particles	Edge: fine acicular transformation product in a matrix of alpha, 0.005 inches; center: equiaxed alpha in transformation matrix, dispersed TiC particles

TABLE 15

OBSERVATIONS OF 950°C. STRIPPED OXIDES OF ALLOY MST 3Al-5Cr

TIME	SIZE	SHAPE	COMMENTS	UNIFORMITY	TYPE MICROGRAPH
30s	8/407	Irregular	Grain boundaries appear white under polarized light, dispersed TiC particles	Fairly uniform	Diffuse, overlapping
45s	8/407	Irregular, small particles	Grain boundaries appear white under polarized light, dispersed TiC particles, small grains appear yellow	Fairly uniform	Diffuse, overlapping
1m	8/407	Irregular, small particles	Grain boundaries appear white under polarized light, dispersed TiC particles, small grains appear yellow	Fairly uniform	Diffuse, overlapping
30m	8/407	Irregular, small particles	Grain boundaries appear white under polarized light, dispersed TiC particles, about 5 per cent small yellow grains	Fairly uniform	Diffuse, overlapping

TABLE 16

OBSERVATIONS ON 700°C. OXIDATION PRODUCTS OF ALLOY MST 3Al-5Cr

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF METAL SAMPLE
10m	Blue-white		Single layer: tenacious, small particles, charcoal with blue cast	Beta in alpha matrix, no evidence of internal oxidation
30m	Blue-white		Single layer: tenacious, small particles, charcoal with blue cast	Beta in alpha matrix, no evidence of internal oxidation
1h	Blue-white		Single layer: tenacious, small particles, charcoal with blue cast	No evidence of internal oxidation, grain growth, beta in alpha matrix
4h	Light-yellow	0.001	Single layer: tenacious, small particles, light gray	No evidence of internal oxidation, grain growth, beta in alpha matrix
15h	Yellow, light-yellow	0.001	Single layer: tenacious, small particles, gray white	No evidence of internal oxidation, coarsening of grain, beta in alpha matrix
30h	Yellow, blue-white	0.001	Single layer: tenacious, small particles, blue-gray	No evidence of internal oxidation, coarsening of grain, beta in alpha matrix
60h	Yellow	0.001	Single layer: tenacious, small particles, sintering with voids and grain growth	No evidence of internal oxidation, beta in alpha matrix, coarsening of grain structure
170h	Orange, light-yellow, green-yellow	0.002	Single layer: tenacious, small particles, sintering with voids and grain growth, blue-gray	No evidence of internal oxidation, beta in alpha matrix, coarsening of grain structure

TABLE 17

OBSERVATIONS ON 700°C. STRIPPED OXIDES OF ALLOY MST 3Al-5Cr

TIME	SIZE	SHAPE	EXAMINATION	UNIFORMITY	TYPE MICROGRAPH
10m	6/1047	Irregular	Mixture of areas containing small grains and large grains, TiC particles	Fair	Diffuse, overlapping
30m	6/1047	Irregular	Polarized light necessary to bring out grain boundaries, transparent showing many small grains, TiC particles present	Fair	Diffuse, overlapping
1h	6/1047	Irregular	Mixture of areas containing small grains and areas containing large overlapping grains, TiC particles present	Fair	Diffuse, overlapping
4h	6/1047	Irregular	Areas containing small light yellow particles surrounded by areas containing small black particles, TiC particles present	Fair	Diffuse
60h	6/1047	Irregular	Polarized light necessary to bring out grains, TiC particles present, particles appear orange	Fair	Diffuse, overlapping

TABLE 18

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2Al-2Fe

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
30s	Blue-white		Outer layer: adherent small particles that can be scraped off, gray with blue cast; core: tenacious, small particles, gold	Edge: alpha dendrites, 0.003 inches; center: equiaxed alpha in matrix of fine acicular transformation product
45s	Blue-white		Outer layer: adherent small particles that can be scraped off, gray with blue cast; core: tenacious, small particles, gold	Edge: alpha dendrites, layer of fine acicular alpha transformation product, 0.002 inches; center: equiaxed alpha in matrix of fine acicular transformation product
1m	White		Outer layer: adherent, small particles that can be scraped off, gray with blue cast; core: tenacious, small particles, purple	Edge: alpha dendrites, 0.002 inches; center: equiaxed alpha in matrix of fine acicular transformation product
3m	White	0.001	Outer layer: adherent small particles that can be scraped off, gray; core: tenacious, small particles, gold	Edge: fine acicular transformation product in matrix of alpha, 0.002 inches; center: equiaxed alpha in matrix of fine acicular transformation product
5m	White	0.001	Outer layer: adherent, small particles that can be scraped off, gray; core: tenacious, small particles, blue	Edge: fine acicular transformation product in alpha matrix, 0.002 inches; center: equiaxed alpha in matrix of fine acicular transformation product

TABLE 18

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST2Al-2Fe

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
8m	Yellow, white	0.001	Outer layer: adherent, small particles that can be scraped off, gray with yellow cast; core: tenacious, small particles, purple and gold mixture	Edge: fine acicular transformation product in alpha matrix, 0.003 inches; center: equiaxed alpha in matrix of fine acicular transformation product
12m	Yellow, white	0.001	Outer layer: adherent, small particles that can be s craped off, gray with yellow cast; core: tenacious, small particles, purple and gold mixture	Edge: fine acicular transformation product in alpha matrix, 0.003 inches; center: equiaxed alpha in matrix of fine acicular transformation product
30m	Orange, white	0.002	Outer layer: loosely adherent, friable, sintering with voids and grain growth, fissures, light yellow; core: tenacious, small particles, charcoal and gold mixture	Edge: fine acicular transformation product in alpha matrix, 0.005 inches; center: equiaxed alpha in matrix of fine acicular transformation product
2h	Orange, white	0.002	Outer layer: nonadherent, friable, sintering with voids and grain growth, fissures, light yellow; core: tenacious, small particles, charcoal	Edge: alpha layer, 0.001 inches; center: equiaxed alpha in matrix of fine acicular transformation product
5h	Orange, yellow, white	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: brown with charcoal spots, underside: small loose particles, white; core: tenacious, small particles, charcoal and some white	Edge: alpha layer, 0.001 inches; center: equiaxed alpha in matrix of fine acicular transformation product

TABLE 18

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2Al-2Fe

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
9h	Orange, yellow, white	0.002	Outer layer: nonadherent, brittle, fissures, sintering with voids and grain growth, surface: brown with charcoal spots, undersurface: small loose particles, white; core: tenacious, small particles, charcoal with some white	Edge: alpha layer, 0.002 inches; center: fine acicular transformation product
15h	Orange, yellow, gray-white	0.004	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: brown with charcoal spots, underside: small loose particles, white; core: tenacious, small particles, charcoal with some white	Edge: equiaxed alpha layer, 0.005 inches; center: fine acicular transformation product in an alpha matrix
18h	Dull orange, dull yellow, charcoal	0.005	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: brown with purple cast, underside: tenacious small loose particles, white; core: tenacious, small particles, charcoal with some white	Fine acicular transformation product in alpha matrix

TABLE 18

OBSERVATIONS ON 950°C. OXIDATION PRODUCTS OF ALLOY MST 2Al-2Fe

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF SAMPLE
20h	Dark blue, very dull yellow, blue-white	0.006	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: slate-gray, underside: small loose particles, blue-gray; core: tenacious, small particles, charcoal with some white	Fine acicular transformation product in alpha matrix
21½	Dark blue, blue-white	0.007	Outer layer: nonadherent, brittle, sintering with voids and grain growth, surface: slate-gray, underside: small loose particles, blue-gray; core: tenacious, small particles, charcoal with some white	

TABLE 19

OBSERVATIONS ON 950°C. STRIPPED OXIDES OF ALLOY MST 2Al-2Fe

TIME	SIZE	SHAPE	COMMENTS	UNIFORMITY	TYPE MICROGRAPH
30s	8/407	Irregular	Very difficult to determine grain structure, dispersed TiC carbides	Fairly uniform	Medium sharp
45s	8/407	Irregular	Difficult to ascertain grain structure, dispersed TiC particles present	Fairly uniform	Medium sharp, overlapping
3m	6/407	Irregular	Gray under polarized light, small particles appear white, dispersed TiC particles	Fairly uniform	Medium sharp, overlapping
5m	6/407	Irregular	Gray under polarized light, 10-20 per cent small particles appear white under polarized light	Fairly uniform	Medium sharp, overlapping
8m	6/407	Irregular	Gray under polarized light, 10-20 per cent small particles appear white under polarized light, dispersed TiC particles	Fairly uniform	Medium sharp, overlapping

TABLE 20

OBSERVATIONS ON 700°C. OXIDATION PRODUCTS OF ALLOY MST 2Al-2Fe

TIME	POLARIZATION COLORS	THICKNESS (INCHES)	FILM CHARACTERISTICS	METALLOGRAPHIC DESCRIPTION OF METAL SAMPLE
30m	Blue-white		Single layer: tenacious, small particles, charcoal with blue cast	No evidence of internal oxidation, beta dispersed in an alpha matrix
1h	Blue-white		Single layer: tenacious, small particles, charcoal with blue cast	No evidence of internal oxidation, beta particles in alpha matrix
4h	Light-yellow	0.001	Single layer: tenacious, small particles, blue-gray	No evidence of internal annealing oxidation, beta in alpha matrix
15h	Light-yellow, blue-white	0.001	Single layer: tenacious, small particles, gray	No evidence of internal oxidation, beta in alpha matrix
30h	Light-yellow, blue-white	0.001	Single layer: tenacious, small particles, gray	No evidence of internal oxidation, beta particles in alpha matrix
60h	Light-yellow, blue-white	0.002	Single layer: tenacious, small particles, light yellow and gray mixture	No evidence of internal oxidation, beta particles in alpha matrix, structure coarsening
170h	Orange, light-yellow, blue-white	0.002	Single layer: tenacious, small particles, yellow, sintering	Thin alpha layer, beta in alpha matrix, structure coarsening

TABLE 21

OBSERVATIONS ON 700°C. STRIPPED OXIDES OF ALLOY MST 2Al-2Fe

TIME	SIZE	SHAPE	EXAMINATION	UNIFORMITY	TYPE MICROGRAPH
10m	6/1047	Irregular, some round	Few large gray and white grains, many small particles appear gray and white under polarized light	Non-uniform	Diffuse
30m	5/1047	Irregular, angular	TiC particles, many large grains isolated around TiC particles	Fairly uniform	Diffuse, overlapping
1h	6/1047	Irregular	TiC particles, many gray particles surrounded by a matrix of blue particles	Fairly uniform	Diffuse, overlapping
4h	7/1047	Irregular	TiC particles, small gray particles surrounded by a matrix of blue particles	Fairly uniform	Diffuse, overlapping
15h	7/1047	Irregular	TiC particles, small areas of gray particles surrounded by a matrix of blue particles	Fairly uniform	Diffuse

TABLE 22

X-RAY DIFFRACTION PATTERNS

MST3Al-5Cr 20 Hrs. 950°C.		RC130A 20 Hrs. 950°C.		MST2.5Fe-2.5V 20 Hrs. 950°C.		MST2Al-2Fe 18 Hrs. 950°C.		MST111 9 Hrs. 950°C.		Rutile (2o)	
d (A)	I*	d (A)	I	d (A)	I	d (A)	I	d (A)	I	d (A)	I
3.22	S	3.21	S	3.21	S	3.20	S	3.21	S	3.245	100
2.47	MS	2.47	M	2.47	MS	2.46	MS	2.47	MS	2.489	41
2.29	F	2.27	VF	2.28	VF	2.27	F	2.29	F	2.297	7
				2.25	VF						
2.17	M	2.17	MF	2.18	M	2.16	M	2.18	M	2.188	22
2.04	F	2.04	F	2.05	F	2.03	F	2.05	F	2.054	9
1.68	S	1.68	VS	1.68	VS	1.68	VS	1.68	S	1.687	50
1.62	M	1.62	M	1.62	M	1.61	MS	1.62	M	1.624	16
1.47	MF	1.47	MF	1.49	MF	1.47	MF	1.47	F	1.480	8
1.45	MF	1.45	MF	1.45	MF	1.45	MF	1.45	F	1.453	6
1.36	MS	1.36	MS	1.36	M	1.35	MS	1.36	MS	1.360	16
1.34	MF	1.34	M	1.34	MF	1.34	M	1.34	MF	1.347	7
1.30	VVF									1.305	1
1.24	F	1.24	VF	1.24	VF	1.24	F	1.24	VF	1.243	3
1.20	VF	1.20	VF			1.19	VF			1.200	1
1.17	MF	1.17	F	1.17	F	1.17	MF	1.17	F	1.1700	4
1.15	F	1.15	F	1.15	VF	1.14	F	1.15	F	1.1485	4
										1.1329	1
1.09	M	1.09	MF	1.09	MF	1.09	M	1.09	M	1.0933	4
1.08	F	1.08	F	1.08	F	1.08	F	1.080	F	1.0827	4
1.041	MF	1.042	MF	1.041	F	1.041	MF	1.041	F	1.0424	5
1.035	MF	1.036	MF	1.036	F	1.034	MF	1.036	F	1.0361	4
1.025	F	1.026	F	1.026	F	1.024	F	1.025	VF	1.0273	3
0.963	VF	0.964	VF	0.964	VF	0.962	F	0.963	VF	0.9642	2
0.906	F	0.907	F	0.907	VF	0.905	F	0.906	F	0.9071	3
0.900	F	0.901	F	0.900	F	0.899	F	0.899	F	0.9007	3
0.889	M	0.889	M	0.889	MF	0.888	M	0.888	M	0.8892	5
0.877	M	0.878	MF	0.878	F	0.876	MF	0.877	MF	0.8773	6
		0.863	F			0.873	MF	0.873	MF	0.8739	5
0.843	F	0.844	F	0.844	F	0.843	MF	0.843	MF	0.8437	5
0.829	MF	0.829	MF	0.830	F	0.828	MF	0.829	MF	0.8290	5
0.819	M	0.820	M	0.819	MF	0.819	M	0.819	MS	0.8196	8
0.780	MF	0.780	MF	0.780	F	0.780	MF	0.780	M		

* Intensities of the lines were visually estimated on the following scale: VS - very strong, S - strong, MS - medium strong, M - medium, MF - medium faint, F - faint, and VF - very faint.

TABLE 22

X-RAY REFLECTION PATTERNS

MST3Al-5Cr 170 Hrs. 700°C.		MST2.5Fe-2.5V 170 Hrs. 700°C.		MST2Al-2Fe 170 Hrs. 700°C.		RC130A 170 Hrs. 700°C.		MST111 170 Hrs. 700°C.		MST111 3 Min. 950°C.		MST111 1 Min. 950°C.		Titanium (19)	
d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I
3.24	100	3.24	83	3.24	68	3.24	100	3.26	100	3.23	15	3.23	10		
2.48	12	2.48	58	2.48	32			2.49	17	2.47	4	2.47	2	2.557	30
								2.38	11					2.342	26
		2.30	6	2.29	4			2.29	12						
		2.27	6	2.26	3			2.26	6					2.244	100
2.18	13	2.19	22	2.18	14			2.18	7	2.18	2				
2.05	6	2.06	6	2.05	5	2.05	12	2.05	13						
								1.74	6					1.726	19
1.69	54	1.69	43	1.69	36	1.68	25	1.68	22	1.68	5	1.68	5		
1.62	24	1.63	12	1.62	9	1.62	54	1.62	18	1.62	1	1.62	2		
1.48	1	1.48	14	1.48	12	1.48	22	1.48	5					1.475	17
1.45	2	1.46	5	1.45	4			1.45	9						
1.36	9	1.36	11	1.36	10	1.36	5	1.36	10	1.36	2				
1.34	2	1.35	12	1.35	8			1.35	9			1.35	2		
								1.348	7					1.332	16
				1.17	2	1.17	7								

TABLE 23

SPECTROGRAPHIC ANALYSIS OF SUPERFICIAL OXIDES GROWN AT 950°C.*

ELEMENT	MST2.5Fe-2.5V	MST3Al-5Cr	RC130A	MST111
	20 Hours 950°C.	20 Hours 950°C.	20 Hours 950°C.	20 Hours 950°C.
V	f			
Sn	W		W	W
Cu	W +	W	W +	W +
Au	t		t	t
Zn	W	W	W	W
Ti	S	S	S	S
Ni	W			t
Pb	W		t	t
Mn	W	t	f	t
Cr	W			
Al	t	t	t	t
Fe	W	t	W	W
Si	W	W	W	W
B	W	t	W +	W +

* The analysis was estimated on the following scale: t 0.001 - 0.01%, w 0.01 - 0.1% and f several 0.1%

TABLE 24

SPECTROGRAPHIC ANALYSIS OF SUPERFICIAL OXIDES GROWN AT 700°C. *

ELEMENT	MST3Al-5Cr	MST2.5Fe-2.5V	MST2Al-2Fe	RC130A	MST111	MST3Al-5Cr
	170 Hours 700°C.	170 Hours 700°C.	170 Hours 700°C.	170 Hours 700°C.	170 Hours 700°C.	18 Hours 950°C.
Al	W	W +	f	t	W	t -
Fe	W	f	f	W +	f -	W +
Si	W	W	W	W	W	W
Sn	t +	t +	t +	t +	t +	t +
Pb	t	t	t	t	t	t
Mn	t -	W	W	W +	W	t -
V		W	W		W -	
Cu	W	f	W +	f	W +	W
Ag	t	t	t	t	t	t
Zn	W	W	W	W	W	t
Ti	S	S	S	S	S	S
Ni	?	W	W	t -	W	
Cr	W +	t	W		?	
Ca	t	t	t	t	t	t
Mg	t	t	t	t	t	t

* The analysis was estimated on the following scale: t 0.001 - 0.01%, w 0.01 - 0.1% and f several 0.1%

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VITA

Robert Kenneth Wolfe, born in Chattanooga, Tennessee, on September 5, 1929, received his secondary education in the public schools of Chattanooga and the Baylor Military Academy. Education was continued at The University of Chattanooga which he attended for two years. An additional two years at the Georgia Institute of Technology culminated with the author being awarded the Bachelor of Chemical Engineering Degree. Since that time, 1951, the author has pursued studies leading to the Doctor of Philosophy Degree in the School of Chemical Engineering.

While at Georgia Institute of Technology the author was, among other things, a member of the honorary research society, Sigma Xi, President of the honorary fraternity, Phi Lambda Upsilon, Vice President of the Graduate Club and the Graduate Student Council, and Secretary of the social fraternity, Pi Kappa Alpha.

Also, at the Georgia Institute of Technology, Mr. Wolfe was a Research Fellow for two years on the Tennessee Eastman Fellowship. In addition, he taught metallurgy and was a Graduate Assistant in the Chemical Engineering Department. He was a Research Assistant at the Engineering Experiment Station of the Georgia Institute of Technology.

In August, 1955, Mr. Wolfe became affiliated with the Engineering Department of the Mallinckrodt Chemical Works.